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Some relaxation studies of molecular and intramolecular motions in glassy o-terphenyl

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SOME RELAXATION STUDIES OF MOLECULAR AND INTRAMOLECULAR MOTIONS MAINLY IN GLASSY o-TERPHENYL

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MASTER OF SCIENCE

1982

D E D I C A T I O N

To my Father

'Faith is a higher
faculty than reasoning'
Philip James Bailey, Festus

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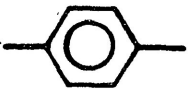
ABSTRACT

In this work, the results of dielectric studies carried out on a number of molecules of the general form  are presented. These molecules have been studied mainly in two forms: as solutions of glassy o-terphenyl, Santovac®, or atactic polystyrene, and in some cases as the pure compressed solid. It is in this latter regard that a new technique for the study of compressed solid preparation has been developed. Studies were carried out over the frequency range 10^2 to 10^5 Hz using a General Radio 1615A Capacitance Bridge.

The experimental data as a function of frequency at different temperatures were analyzed by computer and fit to the Eyring rate equation. From this analysis, activation energy barriers for the observed dielectric relaxation processes were obtained.

Molecules studied have been chosen to correlate such properties as symmetry and electronic and steric effects to the observed Eyring rate parameters.

Similarly, the medium of study (i.e. molecular glass, macromolecular glass or as a compressed solid) has been varied when possible to effect a more complete separation between overlapping molecular and intramolecular relaxation processes.

The latter aspect of this thesis, Chapter VI, discusses results obtained in the study of a number of interesting bridged diaryl molecules.

Inasmuch as glassy o-terphenyl is a relatively untested solvent, a variety of carefully chosen rigid molecules was studied in an attempt to better understand the constraints placed on molecular motion within it. These results have been recorded and discussed in Chapter IV of this thesis.

C H A P T E R I

CHAPTER I

INTRODUCTION

In the early years of dielectric studies, most research was carried out in radiowave frequency, then later on in the microwave regions of the electromagnetic spectrum. A wide variety of polar solutes was dispersed mainly in non-polar solvents of varying viscosities and studied at microwave frequencies. It was soon apparent that viscosity played an important role in the behavior of these polar solute molecules in applied electric fields, and, therefore, solvents of varying viscosities were investigated to determine the effects on the dielectric relaxation properties of dilute dipolar solutions.

As time moved on, solutions of ever increasing viscosity were found and, with the advent of the polymer sciences, systems of extremely high macromolecular viscosities were made with polymers as solvents where the solute at low concentration was dispersed in the polymer [1,2]. One of the most commonly used polymeric solvents

is polystyrene. Since polystyrene has, below its glass transition temperature, very little dielectric loss of its own, its dielectric interference with the dispersed material under study is minimal. Polystyrene samples over the frequency range 100 Hz to 1 GHz have loss factors which are less than $1x10^{-3}$.

One factor which has concerned researchers over the years has been the free volume contained within these polymeric matrices [3]. In cases where flexible molecules, that is to say molecules capable of both molecular and intramolecular relaxation processes, have been studied, there has been direct evidence showing that the magnitude of the barrier to molecular motion may be sufficiently raised so as to allow complete separation and hence observation of the two independent processes.

The search for systems with less free volume has continued as it is reasoned that as the dielectric solutions density increases, the more free-volume conscious molecular process becomes more constrained. Hence, the ability to separate molecular and intramolecular

processes within the same sample should become more feasible.

One such technique which was developed, in the hope that complete molecular motion could be arrested while allowing the less volume dependent group relaxation to carry on, was that of compressed solid formation. Several researchers, including this author, have used this technique. [4]

In the past twenty years, macromolecular glasses have been used to study mainly group rotation in flexible molecules as previously stated. Such has been the case with the acetyl group. [5,6] While a certain degree of success has been obtained in separating the group from the molecular process [4], some molecules that have been studied have been resistant to such viscosity related separation; that is to say the molecular and intramolecular processes overlap. This occurs when the free energy of activation, ΔG_E, for the group and molecular processes are of the same order and so occur over the same temperature and frequency ranges.

Again, it was for these types of molecules that another solvent system was sought. They are referred to as molecular glass-forming systems and include such molecules as o-terphenyl, decalin, and Santovac®. It is felt that by the monomolecular nature of these compounds, even tighter packing arrangements could be achieved, thus restricting further the molecular motion of the dipolar solute dispersed within them.

One of these systems, o-terphenyl, has been studied as liquid solutions [7], super-cooled liquids [9], and more recently, as solutions below its glass transition temperature, Tg [5].

One of the primary aims of this author is to establish the nature of the molecular glass, o-terphenyl. This has been accomplished by a careful study of a number of rigid molecules of increasing molecular volume monomolecularly dispersed within the glassy structure. As well, the dielectric behavior of the pure solvent itself, o-terphenyl, (see Figure I-1) has been studied from liquid nitrogen temperatures up to the glass transition temperature, Tg, of ∿343 K.

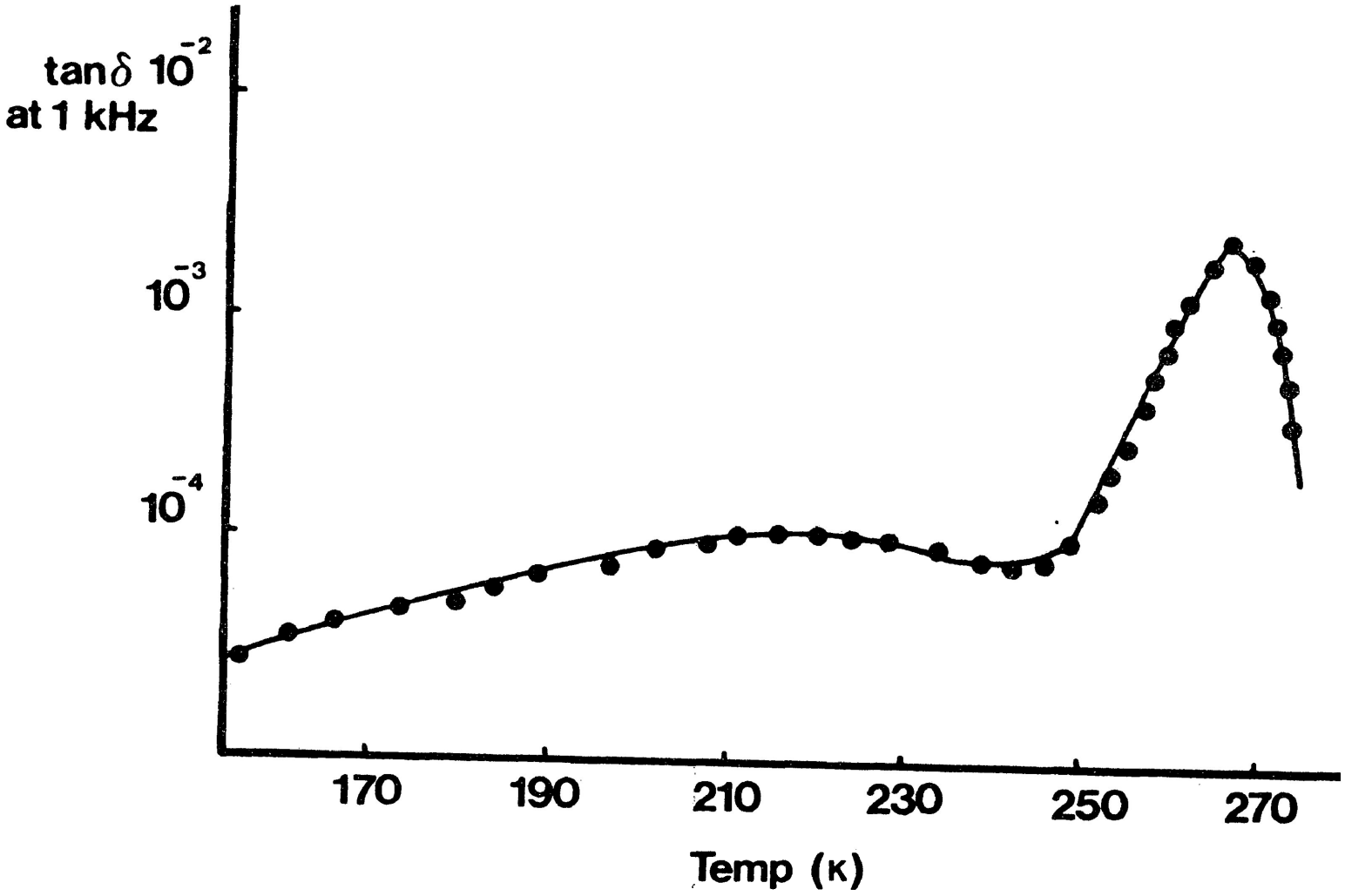


Figure I-1 Loss versus temperature for pure glassy o-terphenyl

In order to gain some insight into the behavior of molecules in this relatively new solvent system, a number of flexible molecules has also been studied in glassy o-terphenyl and in some other solvents to see what trends, if any, might be observed for their molecular and intramolecular motions. These comparisons have been made primarily between the Eyring parameters observed for largely acetyl-containing molecules in glassy o-terphenyl and other solvent systems.

The secondary, and perhaps more novel study has been that of a number of symmetric and asymmetric bridged diaryl molecules in several solvents. Through the study of benzophenone and a closely related analogue of benzophenone, 2,3,4,5,6-pentadeuterobenzophenone, a rather interesting comment may be made concerning the somewhat controversial manner in which these, and perhaps like molecules, demonstrate such anomolously short relaxation times. The two major mechanistic views, namely double-internal rotation as put forth by Fong [10] and that of a mesomerically induced dipolar reorientation, [11,12] are examined experimentally and theoretically [13] with, at least in the case of benzophenone, the intent of understanding further the mechanisms through which it may relax.

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C H A P T E R II

CHAPTER II

BASIC THEORY

At microwave and the radiowave frequencies, molecular and intramolecular processes are observable in various temperature ranges. It is in these two regions that the bulk of dielectric relaxation studies has been carried out. Figure II-1 outlines the various regions within the electromagnetic spectrum.

Dielectric Materials

Dielectric materials are of two fundamental types and are characterized by the absence of free charge able to move through the material under the influence of an applied electric field.

In non-polar dielectrics, all electrons are bound, and so the only motion possible in the presence of an electric field is a very limited displacement of positive and negative charge in opposing directions. The normally non-polar molecules now possess induced dipole

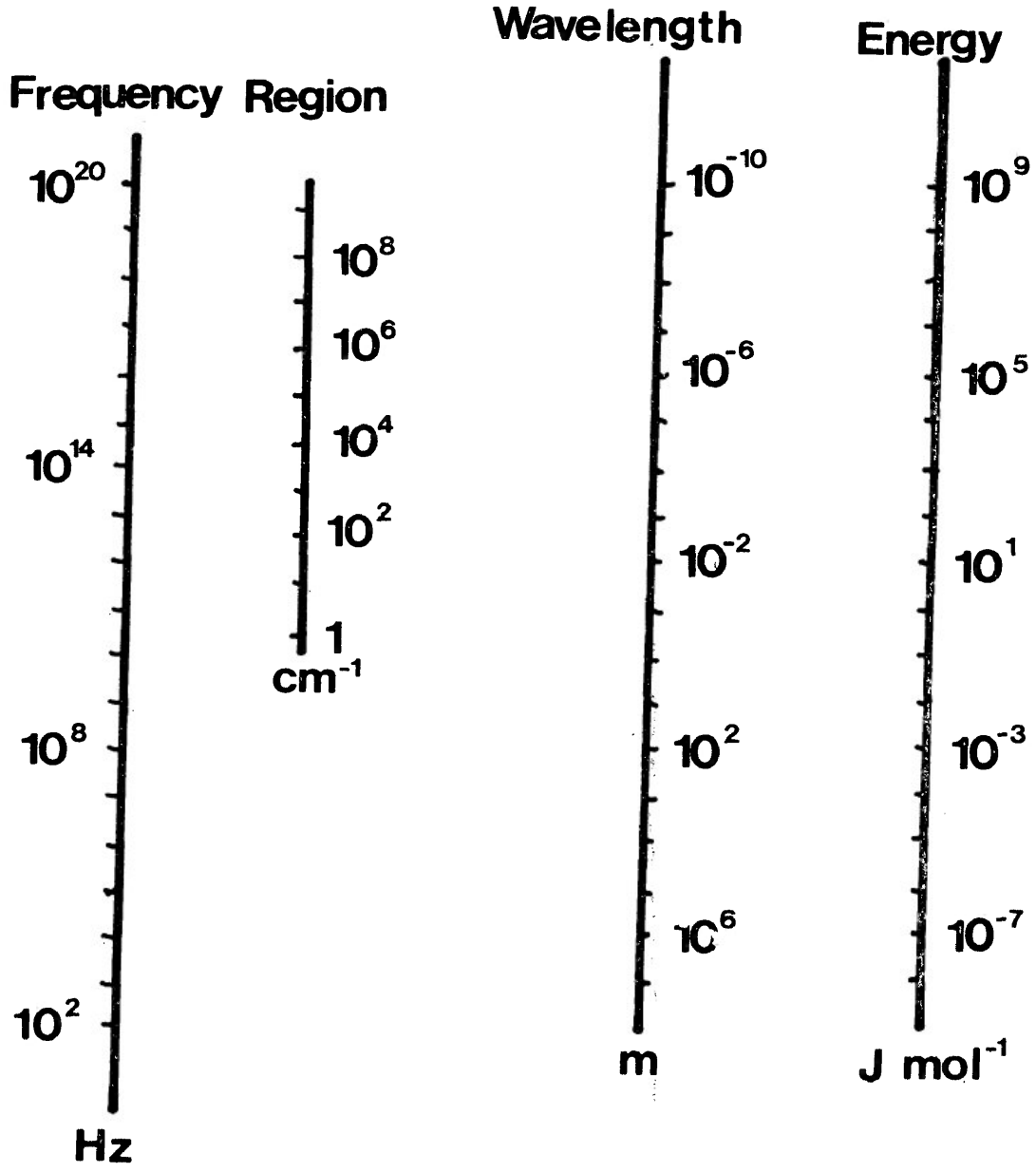

Figure II-1 Frequency, wavelength, energy diagram.

moments, and the material is said to be polarized.

In the case of polar dielectric materials, the sum of the positive and negative charges is zero, and so the molecules are electrically neutral. The distribution of these charges is such that the positive and negative charges are separated by a distance of molecular dimension. The dipole can be described as being made up of charges ^{+}q and ^{-}q separated by a distance d. The dipole moment for such a displacement of charge then is qd.

When the magnitude of the charges is taken to be 10^{-10} e.s.u. and the separation distance as 10^{-8} cm, the dipole moment will be of the order of 10^{-18} e.s.u. which is referred to as a Debye unit.

The magnitude of a dipole moment depends upon a number of factors. Within a given molecule there may be a number of individual dipole moments which, depending upon the size, symmetry, and even nature of the attached substituents, will result in overall or net dipole moments which are quite large or small.

The total polarization (P_T) of a dielectric material in an applied electric field can be described by the Clausius-Mossotti-Debye theories [1] as:

$$P_T = P_E + P_A + P_O = \frac{4\pi N}{3}\left(\alpha_E + \alpha_A + \frac{\mu^2}{3kT}\right)$$

$$= \frac{\varepsilon_o - 1}{\varepsilon_o + 2}\left(\frac{M}{\rho}\right) \qquad \text{II-1}$$

where
- ε_o ... static dielectric constant
- M ... gramme formula weight
- ρ ... density of the material
- N ... Avogadro's number
- α ... polarizability factor
- μ ... electric dipole moment
- k ... Boltzmann constant
- T ... absolute temperature

P_E, the electronic polarization factor, is the contribution due to the relative displacement of the nuclei and electrons and is one of the factors contributing to the total polarization (P_T) described by the preceding equation (II-1). The other two, P_A and P_O, are the con-

tributions of the atomic component resulting from the relative displacement of atoms within a molecule and the orientational component, which arises from dipolar alignment with the applied electric field, respectively.

The bulk of this study will focus on polar dielectric materials and their interaction with applied alternating electric fields in liquids and solids.

While the Clausius-Mossotti-Debye [1] theories are applicable to gases, they are generally inadequate when applied to polar liquids owing to the inability of the Lorentz field used in these theories to represent adequately the local field in a dipolar dielectric.

Onsager, [2] in an attempt to extend the relation between permittivity and dipole moment in liquids and solids, developed the following expression:

$$\frac{(\varepsilon_o-\varepsilon_\infty)(2\varepsilon_o+\varepsilon_\infty)}{\varepsilon_o(\varepsilon_\infty+2)^2}\ \frac{M}{\rho} = \frac{4\pi N\mu^2}{9kT} \qquad \text{II-2}$$

where ε_∞ is the dielectric constant at very high frequencies

when the orientation polarization component vanishes.

Equation II-1 now becomes:

$$\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} \frac{M}{\rho} = \frac{4\pi N}{3} (\alpha_E + \alpha_A) \qquad \text{II-3}$$

On combination of equations II-1 and II-3 the Debye equation II-4 results:

$$\frac{3(\varepsilon_o - \varepsilon_\infty)}{(\varepsilon_o + 2)(\varepsilon_\infty + 2)} \frac{M}{\rho} = \frac{4\pi N \mu^2}{9kT} \qquad \text{II-4}$$

In order to compare the values of μ^2 as determined by Onsager and Debye, one compares equations II-2 and II-4 to give:

$$\frac{\mu^2(\text{Onsager})}{\mu^2(\text{Debye})} = \frac{(2\varepsilon_o + \varepsilon_\infty)(\varepsilon_o + 2)}{3\varepsilon_o(\varepsilon_\infty + 2)} \qquad \text{II-5}$$

As is the case with gases at low pressure, ε_o and ε_∞ are nearly identical and so the Onsager equation reduces to the Debye equation.

The dielectric constant or permittivity of a material can be expressed in terms of its polarizability which is a function of the frequency of the applied field. For the majority of normal-sized polar molecules in non-polar solvents, the three components of P_T, namely P_E, P_O, and P_A, can all reach their equilibrium values when the applied field is of the order of 10^8 Hz or less. As the frequency of the applied field increases, the dipoles begin to lag behind and the polarization (P_O) falls off so that its contribution to the total permittivity decreases. It is this decrease in polarization and permittivity and the resultant absorption of energy which describes the dielectric dispersion. This phase difference between the applied field and the dipolar reorientation causes a dissipation of energy known as Joule heating which is measured by the dielectric loss (ε'') defined below as:

$$\varepsilon'' = \varepsilon' \tan\delta \qquad \text{II-6}$$

where ε' is the real component of the complex term of the dielectric constant and $\tan\delta$ is the loss tangent or energy dissipation factor.

The following equation and diagram represents the complex quantity of the dielectric constant in this frequency region.

$$\varepsilon^* = \varepsilon' - i\varepsilon'' \qquad \text{II-7}$$

where $i = \sqrt{-1}$

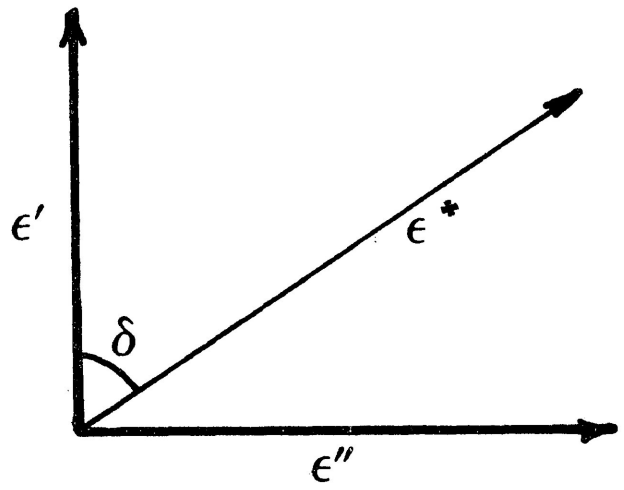

Figure II-2 Loss tangent curve.

The following plot of Total Polarization versus Log Frequency illustrates the absorption region associated with the different polarization mechanisms over the frequency region 10^7 to 10^{13} Hz.

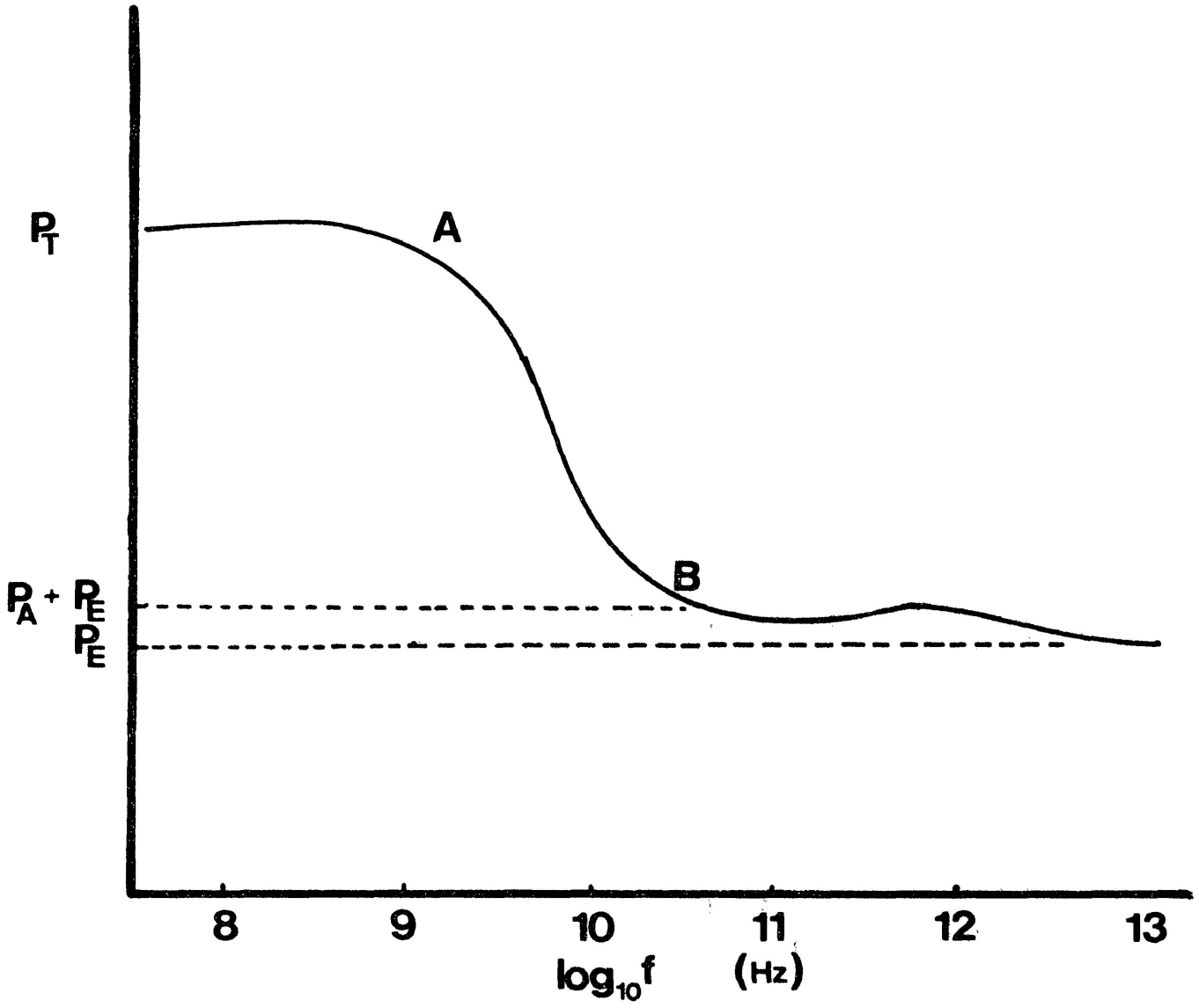

Figure II-3 Polarization curve

Between points A and B on Figure II-3 the total polarization (P_T) decreases expectedly as the dielectric absorption process becomes complex [1]. The entire curve, in fact, describes the absorption

region associated with the different polarization mechanisms observed over a portion of the electromagnetic spectrum. It is, however, over the region A to B that the dipole moment begins to lag behind the applied field. The time required, and hence the frequency corresponding to the region over which the orientational polarization response is observed (since time and frequency are interrelated) may be shown in part to be due to the frictional resistance of the medium to the change in molecular orientation. The larger molecules in a viscous medium will take longer to reorientate themselves than say small molecules in liquids of quite low viscosity.

Dielectric relaxation, one of the key concepts dealt with in this thesis, is the exponential decay with time of the polarization of a dielectric material when an applied external field is removed or, in the case of an alternating field, falls to zero.

The relaxation time, τ, is defined as the time (t) required for an initially polarized population of molecules (P_o) to decay to 1/e times that original

value, hence:

$$P(t) = P_o \exp(-t/\tau) \qquad \text{II-8}$$

where P(t) is the polarization at time t in an electromagnetic field.

For simple systems, the frequency dependence of the complex permittivity is given by:

$$\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_o - \varepsilon_\infty} = \frac{1}{1+i\omega\tau} \qquad \text{II-9}$$

where ε_o and ε_∞ are the static and infinite frequency permittivities respectively. These represent the low and high frequency limiting values of ε^*. ω is the angular frequency in rad s^{-1} and τ is the characteristic relaxation time in seconds defined as the time required for the polarization to decay to 1/e of its initial value when 'e' is the natural logarithmic base q.v..

The static permittivity (ε_o) of a dielectric is the ratio of the capacitance (C) of a condenser to

the capacitance (C_o) of the condenser with a vacuum between the plates, hence:

$$\varepsilon_o = C/C_o \qquad \text{II-10}$$

On combination of equations II-9 and II-10, and on separation into real and imaginary parts, the Debye and Pellat equations result:

$$\frac{\varepsilon' - \varepsilon_\infty}{\varepsilon_o - \varepsilon_\infty} = \frac{1}{1+(\omega\tau)^2} \qquad \text{II-11}$$

$$\frac{\varepsilon''}{\varepsilon_o - \varepsilon_\infty} = \frac{\omega\tau}{1+(\omega\tau)^2} \qquad \text{II-12}$$

where ε_∞ and ε_o are the permittivities above and below the absorption respectively,

$\varepsilon_o - \varepsilon_\infty$ is termed the dispersion factor of the relative permittivity,

ω is the angular frequency in radians per second, and

τ is the relaxation time in seconds of the system.

The relaxation time, τ, of a system can be related to the

position of the frequency maximum in the loss factor curve in the following expressions:

$$\omega\tau = 1$$

and $$\omega = 2\pi f_{max}$$

so $$\tau = \frac{1}{\omega} = \frac{1}{2\pi f_{max}} \qquad \text{II-13}$$

where f_{max} is the frequency maximum of the loss factor curve.

Cole and Cole [3] considered the Debye Equation in the following form:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_o - \varepsilon_\infty}{1 + i\omega\tau} \qquad \text{II-14}$$

and again, on separation into real and imaginary parts, and on combination of equations II-5 and II-6 with subsequent elimination of $\omega\tau$ from these equations, developed the following expression:

$$(\varepsilon' - \frac{\varepsilon_o + \varepsilon_\infty}{2})^2 + \varepsilon''^2 = (\frac{\varepsilon_o - \varepsilon_\infty}{2})^2 \qquad \text{II-15}$$

This equation, which is that of a circle with its centre lying on the abscissa, yields the Cole-Cole plot when ε'' and ε', determined at the same frequencies, are plotted against each other on equal axes.

Since many molecules exhibit a range of, rather than discrete, relaxation times, Cole and Cole [3] modified Debye's original equation to consider a symmetrical distribution of relaxation times about the mean time, τ_o, yielding the following equation:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_o - \varepsilon_\infty}{1 + (i\omega\tau_o)^{1-\alpha}} \qquad \text{II-16}$$

where α is the distribution parameter whose values range $0 \leqslant \alpha \leqslant 1$. The special case of $\alpha = 0$ results in Debye's original expression. An equation similar to II-9 can be derived differing only in the α term which determines the degree to which the centre of the Cole-Cole plot semi-circle is depressed below the abscissa.

Other functions have been considered for non-Debye types of absorption processes. Cole-Davidson have formulated a function to describe right-skewed arcs [4]. The equation is:

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_o - \varepsilon_\infty}{(1+i\omega\tau)^\beta} \qquad \text{II-17}$$

where β is the asymmetric distribution co-efficient.

Another group to propose a theory regarding the distribution of relaxation times in an absorption process was Fuoss and Kirkwood [5]. These workers found that the dielectric loss of some polymers could be represented by the following equation:

$$\varepsilon'' = \varepsilon''_{max}\ \mathrm{sech}(\beta \ln(\nu_{obs}/\nu_{max})) \qquad \text{II-18}$$

where β is an empirical parameter the inverse of which relates to the 1/2 width of the absorption curve taken relative to the Debye process (where $\beta = 1$).

From Fuoss-Kirkwood analysis, ν_{max} and hence the average relaxation time for the process under study

can be obtained from the following equation:

$$\cosh^{-1}\left(\frac{\varepsilon''_{max}}{\varepsilon''}\right) = 2.303\beta(\log\nu_{max} - \log\nu) \qquad \text{II-19}$$

To this point we have considered relaxation times from, on one side, the simplistic discrete Debye approach to, on the other, a number of mathematical functions which attempt to satisfy the seemingly anomolous distribution of relaxation times for a given process [6]. Molecules which contain a rotatable group can have both molecular and intramolecular relaxation processes. This additional variable has posed, from both a theoretical and an experimental point of view, quite a problem.

The dielectric absorption process might be characterized by the "discrete" relaxation times which correspond to molecular and intramolecular motions. Budó [7] suggested the complex dielectric absorption could be represented by the superimposition of overlapping Debye equations for multiple discrete relaxation processes.

The following three equations describe the two

relaxation time processes as:

$$\varepsilon' = \varepsilon_\infty + (\varepsilon_o+\varepsilon_\infty) \left\{ \frac{C_1}{1+\omega^2\tau_1^2} + \frac{C_2}{1+\omega^2\tau_2^2} \right\} \qquad \text{II-20}$$

$$\varepsilon'' = (\varepsilon_o - \varepsilon_\infty) \left\{ \frac{C_1\omega\tau_1}{1+\omega^2\tau_1^2} + \frac{C_2\omega\tau_2}{1+\omega^2\tau_1^2} \right\} \qquad \text{II-21}$$

$$C_1 + C_2 = 1 \qquad \text{II-22}$$

where C_1 and C_2 are weighting factors for the molecular and intramolecular relaxation processes respectively. When C_1/C_2 is small, an almost symmetrical Cole-Cole plot results. Systems with significantly large τ_1/τ_2 and C_1/C_2 ratios may have the two processes separated into two distinct absorption regions. There have, however, been considerable discrepancies in results obtained using this method of analysis in the past with certain molecules, and, since it has not been used as an analytical technique in any of the results presented in this thesis, it will not be discussed in greater detail.

There has been a number of models suggested to account for the relaxation processes of molecules. Debye, who has suggested quite a simple mechanism, proposes two equilibrium positions, equal in energy and opposite in direction for each dipole [1]. These two equilibrium positions, A and A', are separated by an energy barrier, ΔE. In such a situation, the dipoles will normally oscillate within the potential minima but, on occasion, acquire enough energy to jump the barrier. In the absence of an external field, however, the statistical probability of finding the dipoles in either minimum are identical, and so at any given instant both equilibrium positions will be equally populated (see Figure II-4).

Since dielectric relaxations are rate processes, the relaxation time is given to be the reciprocal of a mean rate coefficient. The Arrhenius equation is one such expression to describe this type of process.

The energy barrier from one equilibrium position to another can be obtained from the interdependence of the absorption maximum on the temperature, by the following expression [8]:

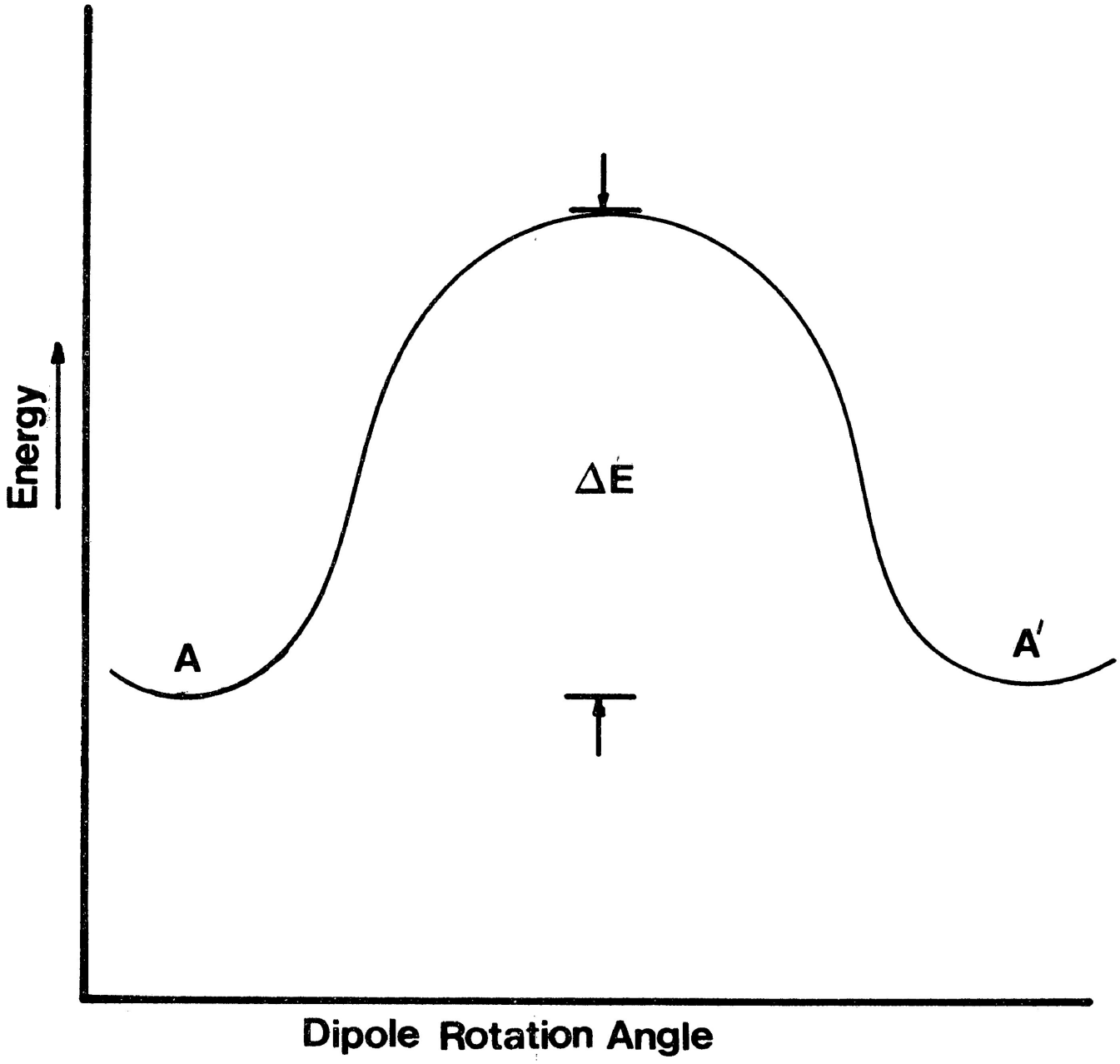

Figure II-4 Plot of Dipole Rotation Angle against Energy (units are arbitrary) for two equilibrium positions A and A' separated by an energy barrier ΔE.

$$f_{max} = \frac{1}{2\pi\tau} = A\exp\left(\frac{-\Delta E}{RT}\right) \qquad \text{II-23}$$

where A is the frequency factor,

R is the universal gas constant which, depending upon the values used, will be in Cal/°-mole or J/°-mole, and

T is the absolute temperature in K.

Eyring in turn developed an equation from which certain thermodymanic parameters can be obtained for processes analogous to chemical rate reactions.

From Eyring's theory the following equation evolved:

$$K_1 = \frac{kT}{h} \exp -\Delta G_E/RT \qquad \text{II-24}$$

where K_1 is a rate constant, and ΔG_E is the free energy of activation,

$K_1 = \frac{1}{\tau}$ the equation becomes:

$$\tau = (h/kT) \exp (\Delta G_E/RT)$$

$$= (h/kT) \exp (-\Delta S_E/R) \exp (\Delta H_E/RT) \qquad \text{II-25}$$

where h is Planck's constant,

ΔS_E is the molar entropy of activation

ΔH_E is the molar enthalpy of activation

τ is the microscopic relaxation time

k is the Boltzmann's constant

R is the universal gas constant, and

T is the absolute temperature.

A plot of $\ln(\tau T)$ versus $\frac{1}{T}$ is a straight line the slope of which yields the enthalpy of activation, ΔH_E, for the observed relaxation process.

Debye [1] in his theory of molecular relaxation likens molecules in the liquid state to spheres rotating in a continuous viscous medium. The relaxation time, τ, for such a system is:

$$\tau = \frac{4\pi\eta a^3}{kT} \qquad \text{II-26}$$

where η is the viscosity

k is the Boltzmann's constant

a is the radius of the molecule, and

T is the absolute temperature.

The Debye equation, II-20, has been modified by Perrin to suit ellipsoidal molecules and is as follows:

$$\tau_i = \frac{4\pi\eta f_i abc}{kT} \qquad \text{II-27}$$

where a,b,c are the lengths of the semi-axes and

f_i is a numerical factor.

It is implicit in these theories that the molecular relaxation process will be affected by the viscosity, apparent or otherwise, of the medium in which the solute is dispersed. Similarly, insofar as the intramolecular process requires considerably less volume (as compared to the molecular process) in which to relax, it should be less sensitive to the viscosity of its surroundings.

One experimental difficulty intrinsic with each of these equations is the viscosity term, η. There is no immediate reason to believe that the microscopic

viscosity of the system, that is to say the viscosity which the molecule actually experiences in situ, is the same as the apparent or macroscopic viscosity of the solution as measured by conventional means. In fact, there is mounting experimental evidence to the contrary and this will be a point discussed in the following chapters.

There does, however, appear to be little doubt that overlapping molecular and intramolecular processes can be, in certain cases, resolved into two separate processes by monomolecularly dispersing the solute in highly viscous media such as molecular [9] or macromolecular non-polar glasses [10,11].

Thus, the aims of the studies reported here are to (1) characterize a relatively new dielectric system, namely glassy o-terphenyl, (2) relate the dielectric behaviour of certain rigid and flexible molecules (or close equivalents) studied in other media to this new solvent system and, finally (3) to gain an insight into the mechanism by which symmetrical diaryl molecules relax.

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C H A P T E R III

CHAPTER III

EXPERIMENTAL PROCEDURES

The majority of the systems studied for this thesis were examined as solutes dissolved in glassy o-terphenyl. At room temperature the solutes were either polar solids or liquids with varying degrees of solubility. Other systems studied included solutes trapped in polystyrene matrices, in the non-polar solvent Santovac® [1], and as the pure compressed solid disk.

Dielectric measurements were made primarily over the frequency range 10^2 to 10^5 Hz using a General Radio Corporation 1615A capacitance bridge in conjunction with General Radio Corporation's 1310-B sine wave signal generator and 1232-A tuneable amplifier-null detector. Actual measurements were made by bringing the bridge into balance as indicated by the null detector for solutions studied in a variety of 3-terminal coaxial and parallel-plate capacitance cells.

The two coaxial cells used operated on basically the same principle but differed radically in design. The two types, referred to as Cell A and Cell B, are illustrated in Figures III-1 and III-2 respectively [2]. Cell B had been designed as a modification of Cell A, to decrease the requisite volume of sample required for study. Also, since the quantity of sample is decreased, it was hoped that the temperature stabilization time would be reduced and that, owing to the closer proximity of the temperature sensors to the sample, the accuracy of the temperature value would be increased. Experimentally, stabilization time, as indicated by the length of time required for the capacitance and dissipation factors of the bridge to reach constant values, has indeed been decreased by this modified cell design. It has also been shown, experimentally, that the temperature differential between the top and bottom of the cell is less than .1 K. This reduces the possibility of inhomogeneity within the sample, particularly at potentially critical phase change temperatures.

The second type of cell, that of a circular

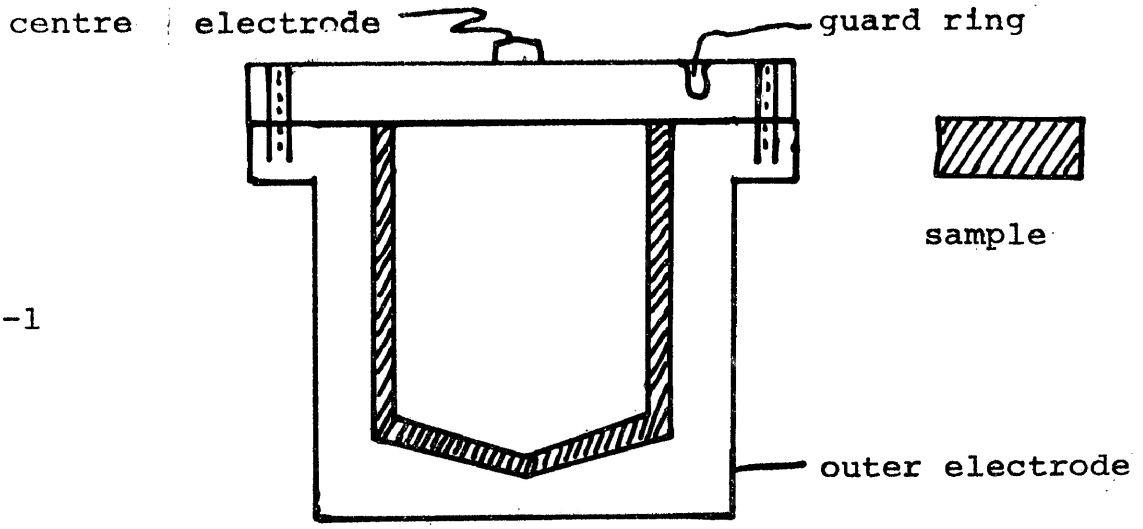
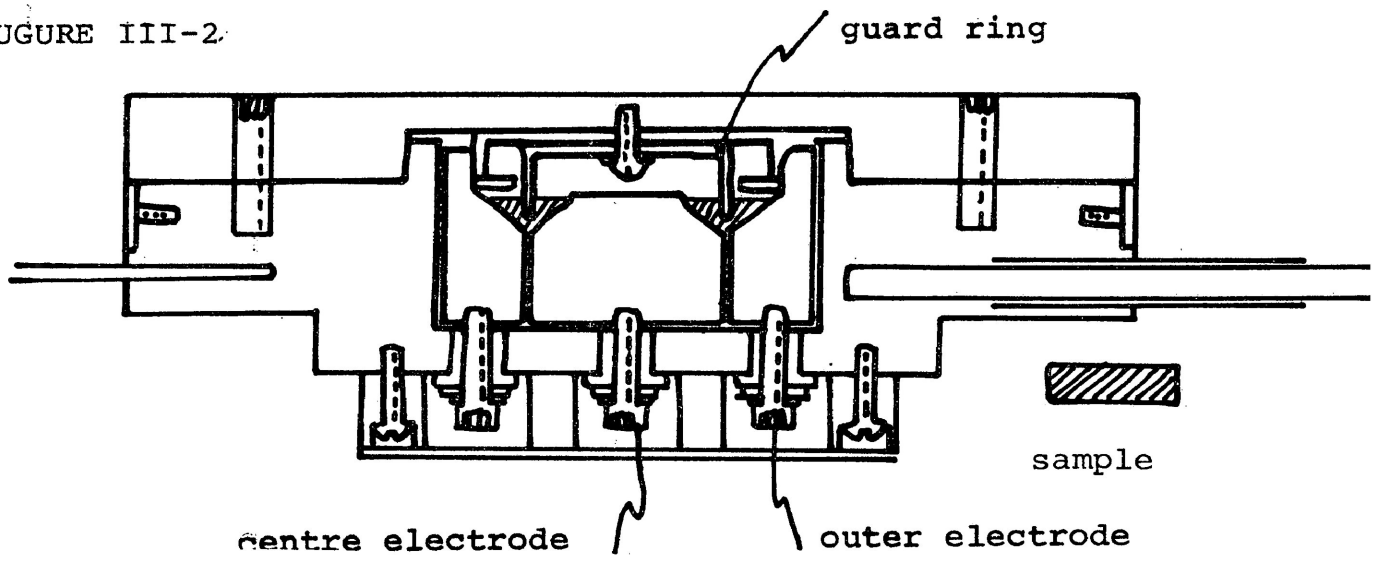


FIGURE III-1

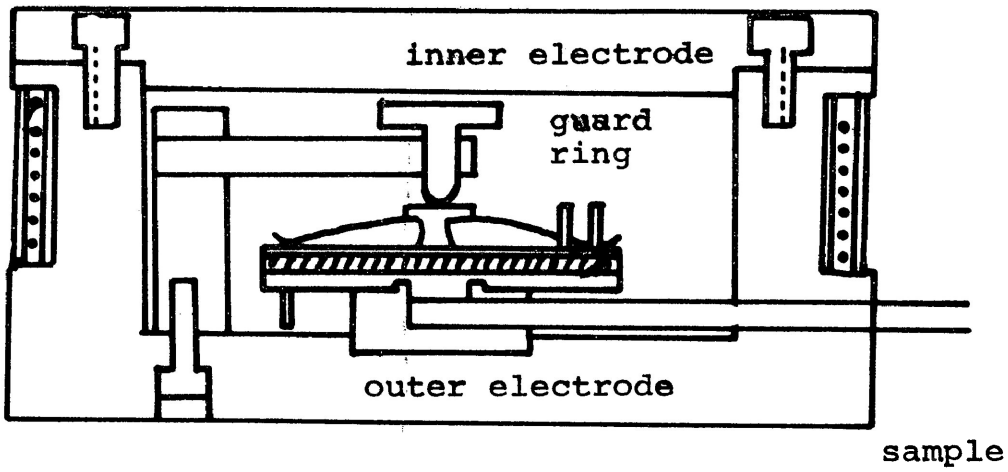
Cell A: Three terminal coaxial cell

FUGURE III-2



Cell B: Three terminal coaxial cell

FIGURE III-3



Parallel-plate capacitance cell

parallel-plate capacitor, is illustrated in Figure III-3 [2]. Two cells were used, having essentially identical characteristics except that the electrode pair in one had been modified so that it could be removed readily from the heating/cooling assembly to accommodate compressed solid disks which, at room temperature, would be unstable.

The capacitance cells, regardless of design, were mounted in essentially the same type of aluminum temperature-controlled container. Each cell was cooled from the top by conduction through a flat-bottomed, styrofoam insulated, liquid nitrogen container. Heating balance was accomplished through a temperature control circuit consisting of a thermocouple, and a thermo electric brand Slectrol® temperature control unit (accuracy $\sim\pm.1°C$) using a nichrome wire heating element surrounding the cell. As well, a suitably accurate, digital temperature probe was located as near to the actual sample as was practical to act as the reference temperature actually used in any of the mathematical evaluations of data.

The practical thermal limits of these systems

were near liquid nitrogen temperatures of 77 K to about 373 K, which is near the melting point of the styrofoam insulation surrounding the total cell assembly [3]. The thickness of the styrofoam surrounding the cell and liquid nitrogen containers was approximately 3.5 cm.

Measurements made with the General Radio bridge were of dissipation or conductivity factors and capacitance. The product of the frequency and dissipation factors yields the loss tangent value, tanδ. With these values obtained experimentally and the following relations, it is possible to determine dielectric loss values for the parallel-plate capacitance cell.

Since $$\varepsilon'' = \varepsilon' \tan\delta \qquad \text{II-6}$$

and $$\varepsilon' = \frac{cd}{.08842A} \qquad \text{III-1}$$

and $$\varepsilon'' = \frac{\varepsilon' G}{\omega c} \qquad \text{III-2}$$

where c is the capacitance of the cell with the sample in picofarads, d is the spacing of the capacitance plates in cm, A is the effective area of the plates, in cm^2, G

is the conductivity of the system in picomohs, and ω is the angular frequency of the applied electric field when frequency is measured in kilohertz, KHz. ($\omega=2\pi\nu$)

Clearly, ε'' may be determined either by conductivity measurements, where equation III-2 applies, or simply as the product of the frequency and dissipation factors which, on combination with equation III-1, are solvable for ε'' using:

$$\varepsilon'' = \varepsilon' \tan\delta \qquad \text{II-6}$$

Both systems were calibrated, to determine relevant constants, by studying samples of precisely known ε' at a given temperature. In the case of the parallel-plate capacitor system, a quartz disk was used, supplied by Rutherford Research Products Co., and having a thickness of .1318 cm and a claimed dielectric constant of 3.819. The coaxial cells were calibrated with purified cyclohexane at room temperature. Calibration studies were initially carried out down to liquid nitrogen temperatures to see if there was any variation between

values of ε' determined at room temperature and those at lower temperatures. Variation was considered negligible.

Sample preparation depended upon a number of factors. Whether the solvent, if indeed a solvent was used, was initially a liquid or solid was the first concern since the solute had to be dispersed within the solvent as a homogeneous solution of relatively low concentration, that is to say less than 8% by weight of solute. The second consideration was the cell type for which the sample was being prepared. Prior to dielectric study, samples for the coaxial cells were liquid, while parallel-plate capacitance samples were pressed from solids.

In the case of solution samples prepared for the coaxial cells, a given polar solute was added to a heated quantity of solvent such that the resultant solution had a weight/weight concentration of approximately 8% or less depending upon the magnitude of the dipole moment of the solute and, in certain cases, on the solubility of the solute in the solvent. The two main solvents used in these studies were o-terphenyl, a glass forming solid with a melting point of approximately 328 K,

and Santovac®, a viscous liquid at room temperature.

To facilitate dissolution of the added solute, and in the case of o-terphenyl, to initially melt the solvent, the Santovac® [1] or o-terphenyl sample was heated to approximately 333 K. The samples were then left twenty-four hours to ensure a homogeneous solution. Once filled with sample, the cells were heated again to above 333 K and then cooled quickly with an aluminum flat-bottomed liquid nitrogen vessel. The cooling rate, depending upon the cell used, was approximately 10 K per minute for cell A and about 18 K per minute for cell B.

In the case of a system, the dielectric characteristics of which were unknown, the sample was taken down to near liquid nitrogen temperature and then slowly heated up to the glass transition temperature while periodic capacitance and dissipation measurements were taken at recorded temperatures. From the resultant plot of tanδ (as calculated from the experimental data) versus temperature (K) at fixed frequency, (usually 1 KHz), suspected areas of dielectric absorption were identified.

The system was then heated up to above 333 K and cooled quickly to some temperature well below that temperature at which the absorption process was expected to be found. Complete, full frequency studies of capacitance and dissipation at specific temperatures were then recorded.

Ideally, these measurements were carried out over the available temperature region to obtain as broad a $\log f_{max}$ range as possible. A discussion of this data will follow in this section.

In the case of solutions of polar solutes dispersed in atactic polystyrene, the samples were prepared in the following fashion:

To a precisely known weight of atactic polystyrene ($\bar{M}wt$ = 240,000) is added approximately 10-15 mL volume of 1,2-trans-dichloroethylene, a non-polar highly volatile solvent. Enough polar solute is then added to the polystyrene/1,2-trans-dichloroethylene solution to make a weight-weight sample of desired concentration between the polar solute and the atactic polystyrene. The

volatile solvent is simply used to dissolve the polystyrene and polar solute and is then boiled off under vacuum in an oven at an elevated temperature. The solution must not be heated so high as to volatilize the solute to be studied. The plastic mass is then weighed to determine the precise concentration of solute dissolved in the solvent on the assumption, of course, that all the trans-dichloroethylene has gone. The sample is then pressed at approximately the melting point of polystyrene i.e. at ∿373 K, at 60000 kPa on a piston in a die to a disk of 4.9 cm diameter.

The resultant disk is then cooled to room temperature in the die, removed, and trimmed to size ready for study. All samples were checked visually for obvious signs of crystallization and flaws. The samples thus prepared were dried over calcium chloride and silica gel for 24 hours to ensure dryness and to allow any mechanical strains to relax prior to dielectric study.

Certain polar molecules have been studied as the pure compressed solid [4]. In the case of molecules, which are solid at room temperature and below, the

sample is simply ground with mortar and pestle to a fine homogeneous powder which is then placed uniformly in the die and compressed at a temperature just below its melting point to a pressure of 120000 kPa. The pressure is then released and the disk recompressed to 240000 kPa and held at this pressure for approximately fifteen minutes. The pressure is then released and the disk removed from the die. The compressed solids, although in certain cases more sensitive to handling than their polystyrene counterparts, were studied in the same fashion as the polystyrene disks using the parallel plate capacitor cell. This technique has been used extensively by other workers in the past [4].

One reason that compressed solid studies were undertaken was that it was felt that the molecular packing of a homo-molecular rather than a hetero-molecular sample might further restrict the molecular motions of flexible molecules, thus virtually eliminating the problems of overlapping molecular and intramolecular processes. It was assumed that the much less volume-dependent intra-molecular process could relax within the available free space present within the normal molecular packing

arrangement for that molecule. One difficulty with this rather successful technique is its obvious limitation to solid samples. It was felt by this author, however, that the vast majority of polar liquids , if reduced to low enough temperatures, could be treated as solids by simply cooling with liquid nitrogen. While this posed a number of experimental difficulties in terms of essentially carrying out the previously described operations at temperatures well below room temperature, they were not unconquerable. It was found that the samples needed generally to be thicker than those used in polystyrene but of the same order as the other pure compressed solid disks made from room temperature solid samples. It was also found that it was easier to form smaller diameter disks, and so a new smaller diameter piston and die set and electrode assembly were constructed. The capacitor assembly was also modified so that the electrodes could be removed easily from the heating/cooling assembly in order that the cold disk could more easily be placed between the two pre-cooled electrodes, thus maintaining the stability of these rather difficult-to-prepare samples. Super-cooled disk samples were stored at temperatures below the melting point of the solid.

In certain cases, the liquids formed glasses on cooling and were more difficult to grind into what was hoped would be an amorphous powder for compression. Also, as the disks were being pressed, it was found that the optimum temperature of the piston and die was just slightly below the melting point of the solid. Thus, as the sample was compressed, there was a tendency, as the pressure rose, for the sample to liquefy within the die and be forced out of the sides of the die assembly. When the pressure on the piston was released, the super-cooled liquid within the die solidified quickly into what is believed to be a glassy structure. The whole die assembly was then cooled well below the melting point of the sample. The die was separated as per usual - see Figure III-4 - and the sample disk placed between the pre-cooled electrode assembly. The complete dielectric capacitor assembly was then placed in the pre-chilled heating/cooling cavity and locked into place. The appropriate connections were made and the unit sealed. Dielectric measurements were then conducted in the previously described fashion.

Certain calculator and computer programmes have

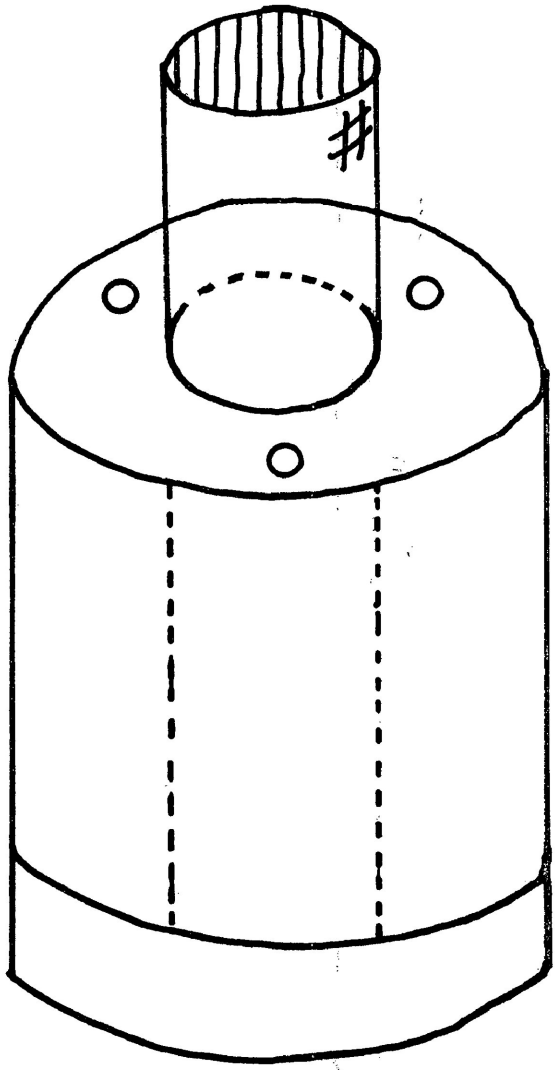


Figure III-4 Piston and die assembly for compressed solids

been written to facilitate the evaluation of experimental data collected using any of the previously described measurement techniques. The programmes written for the various cell types have been included in the appendix section of this thesis. Certain computer programmes written in the APLSF language have also been included and will be described herein [6].

With frequency data and corresponding corrected dielectric loss data as calculated using the Texas Instruments SR59 programmable calculator i.e. $\Delta\varepsilon''$ = ε'' (solution) - ε'' (solvent), the Fuoss-Kirkwood II-1 Equation [7] was evaluated using the APLSF programme titled FUOSSK. This programme which calculates $\Delta\varepsilon''_{max}$, plots the best fit of observed data to the Equation: [8,9]

$$\cosh^{-1}\left(\frac{\Delta\varepsilon''_{max}}{\varepsilon''}\right) \quad \text{versus} \quad \ln(\nu) \qquad \text{III-4}$$

The slope of the line, the frequency of maximum dielectric loss (f_{max}), and the intercept of that line with the $\cosh^{-1}$ axis makes possible the evaluation of the distribution parameter (β). [10]

These two programmes, FUOSSK and EYRING, are both presented in the appendix section at the end of this thesis.

Synthesis of 2,3,4,5,6-pentadeuterobenzophenone

One molecule of particular interest in this thesis is a deuterated analogue of benzophenone. The synthesis, purification, and subsequent analysis of purity are presented below. The synthetic method used is a modification of one used classically to make benzophenone from benzoyl chloride in excess benzene in a Friedel-Crafts acylation reaction [11]. The variation in this case is the substitution of D6-benzene for benzene in the reaction.

In 1958, N. P. Buu-Höi and N.D. Xuong first reported the synthesis of what they described as benzophenone-d_5 [12]. The yields and unambiguous positioning of deuterium in this molecule were not reported. For this reason, the molecule synthesized for this study has been carefully analyzed to determine precisely the positions of the deuterium atoms present and the yield in which the product was formed. All reagents, with the exception of hexadeuterobenzene, were purified prior to use.

Experimental Procedure

To a three necked, five-hundred mL round-bottomed flask, containing a slurry of 20 gm $AlCl_3$ in an excess of hexadeuterobenzene, was added one quarter mole of benzoyl chloride (33.9 gm) at a drop-wise rate over one-half hour at a temperature of 323 K. The temperature of the reaction system was then raised to approximately 353 K and refluxed at this temperature for six hours. The mixture was stirred magnetically over the course of the reaction. The reaction mixture was neutralized with aqueous sodium carbonate and then washed with five, 50 mL portions of petroleum ether (b.p. = 323 K). The hydrocarbon layers were collected and evaporated under vacuum to give 36.5 gm of crude product. Ten grammes of crude acylation products were distilled under a vacuum of approximately 1.0 kPa at a temperature of 423 K. Two fractions were collected, the first being largely benzoic acid co-distilled with a small amount of the deuterated product. The second fraction was a clear liquid weighing 9.5 gm. The overall yield of the deuterated product was calculated to be 74.1%.

Product Identification

The suspected product, 2,3,4,5,6-pentadeutero-benzophenone, was tested using a variety of techniques to confirm its identity. A thin-layer, chromatographic study was carried out on the purified product which, at room temperature (~293 K), is liquid using silica gel as the stationary phase and 1:19 ether/benzene as the eluent. The sample showed, on iodine developing, one clearly defined spot 3.6 cm from the base line. A second thin-layer plate was spotted with the purified product against an authentic sample of benzophenone. In this case, the two resultant spots were found to have virtually identical positions relative to the distance travelled by the ether/benzene eluent. It was felt that the polarities of D5-benzophenone and an authentic sample of benzophenone should be similar, and so the chromatographic evidence tends to suggest that, indeed, the product is benzophenone-like in nature.

Low energy spectrum studies of the deuterated product reveal a molecular ion of 187 mass units whereas pure benzophenone has a molecular ion of molecular

weight 182. The indication is that the product contains 5 deuterium atoms, the precise locations of which can be confirmed by the observed fragmentation patterns.

For example, two peaks are observed at molecular weight of 110 and 105. These may be accounted for in terms of the deuterated and undeuterated acylium ions respectively, characteristic of the loss of a non-deuterated or deuterated phenyl ion. Similarily, two peaks are observed at molecular weights of 77 and 62. These values correspond to the deuterated and non-deuterated phenyl ions from the previously described fragmentation.

A major concern in the synthesis of the molecule was the possibility of a deuterium/hydrogen exchange with hydrogen atoms on the acyl ring or deuterium atoms on the hexadeuterobenzene ring. One possible result of such an exchange on the acyl phenyl ring is:

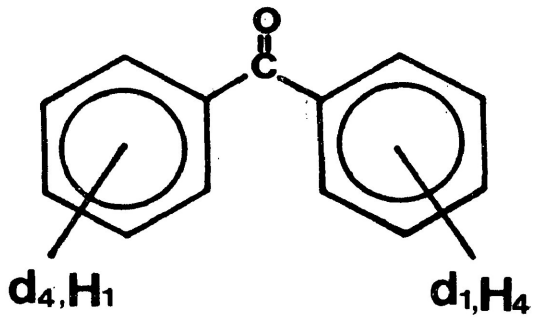


Figure III-5

where the absolute positions of all deuterium atoms are not certain. This molecule would still show a molecular ion at 187 mass units, but there would be subtle changes to the fragments observed from the previously described fragmentation patterns. The acylium ions, (a) and (b) would not be found at precisely 105 or 110 but rather

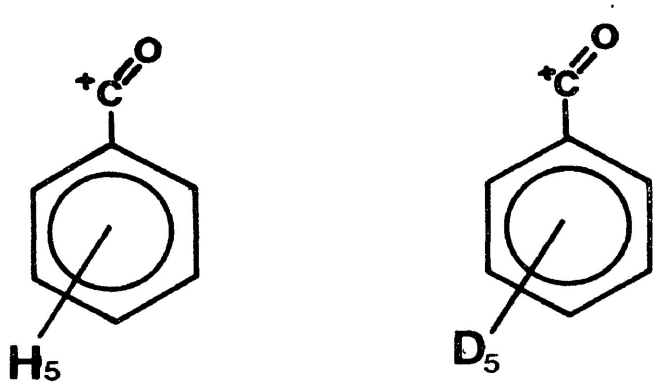


Figure III-6

at 106 and 109 mass units, the two fragments being:

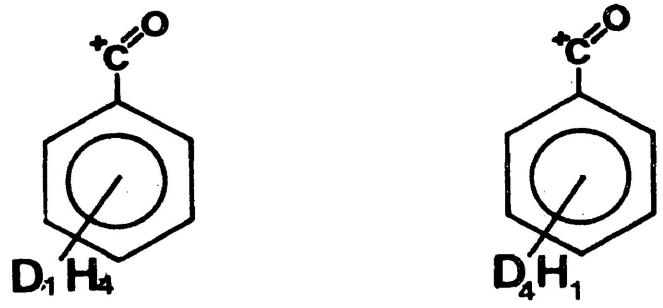


Figure III-7

Similarly, the corresponding phenyl ions expected at 82 and 77 would be at 81 and 76 mass units. Of course, there are a number of other combinations of five deuterium and five hydrogen atoms on ten available sites. These would tend to produce a very complicated mass spectrum.

If there was any loss of deuterium in the molecule, such that the product was not pentadeuterated, multiple molecular ions would be expected. In fact, none of the mass spectrographic evidence is consistent with any loss or intramolecular exchange of deuterium.

Micro elemental analysis of this compound for carbon and hydrogen has proved difficult owing to the relatively high deuterium to hydrogen ratio. Since carbon and hydrogen are measured as a function of differing thermal conductivities of carbon dioxide and water, assuming normal isotopic distributions of carbon and hydrogen, the constants used in relating the conductivities in μV to mass carbon and hydrogen in μgm must be examined more closely.

The normal isotopic distribution, in the case of carbon, has remained unchanged, and so the weight of carbon in the sample as determined by elemental analysis and hence the percent carbon by weight for the molecule can be considered reliable. The theoretical percentage of carbon expected to be found in 2,3,4,5,6-pentadeutero-

benzophenone differs by less than one percent of the calculated value, (83.43% theoretical versus 82.77% observed).

On consideration of the apparent hydrogen percentage, the instrument is unable to distinguish between the thermal conductivities of the three possible combustion products containing hydrogen or deuterium, namely D_2O, DHO, and H_2O. Inasmuch as deuterium is twice the weight of hydrogen, the constant used to relate the thermal conductivity of 'water' resulting from combustion of the sample is not valid. For this reason, only carbon determinations have been used and these support the thirteen carbon structure represented below as Figure III-8.

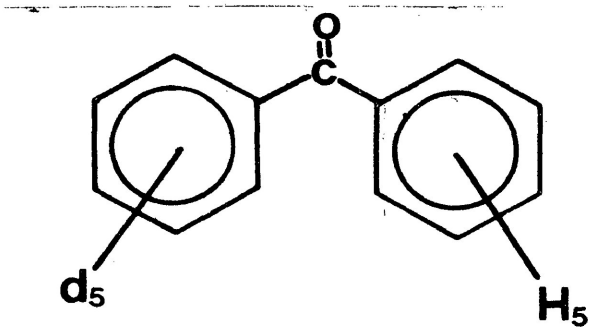


Figure III-8 2,3,4,5,6-pentadeuterobenzophenone

All molecules studied by this author, with the exception of two, were prepared commercially. The two molecules prepared in this laboratory, 2,3,4,5,6-pentadeuterobenzophenone and bis(p-tolyl) sulfide, were synthesized by the author and Dr. M. A. Desando [12] respectively.

REFERENCES CHAPTER III

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C H A P T E R IV

CHARACTERIZATION AND RELAXATION STUDIES OF SOME RIGID MOLECULES IN GLASSY o-TERPHENYL

CHAPTER IV

INTRODUCTION

Over the years, investigators have been interested in the challenge of interrelating dielectric relaxation processes with such factors as entropy of activation (ΔS_E), the size and shape of rigid dipolar molecules, and the probable volumes swept out by these molecules during their reorientation process, also with moments of inertia, viscosity of the medium, and the direction of the dipole within the molecules.

Rigid molecules have been studied in order to determine what, if any, molecular contribution could be expected in similar sized flexible molecules.

Higasi [1] showed an almost linear dependence of ΔS_E on the enthalpy of activation (ΔH_E) for a variety of organic molecules in p-xylene. Tentatively, he postulated that, "the entropy change is zero or has a small negative value, if ΔH_E is below 13.4 kJ mol^{-1}".

Kalman and Smyth [2] studied 2,2-dichloro and 2,2-dinitropropane, camphor, 1-chloronaphthalene, isoquinoline, 4-bromo biphenyl, and acridine in Nujol solutions at 293, 313, and 333 K. For these molecules, ΔH_E and ΔS_E of 6.7, 8.3, 10.1, 15.2, 18.9, 37.6, and 45.9 kJ mol^{-1} in the former and -0.6, -0.7, -1.2, .5, 4.0, 11.5, and 19.8 J K^{-1} mol^{-1} in the latter case were observed. The increase in the enthalpies and entropies of activation between spherically shaped molecules and more elongated ones is in keeping with the results previously reported by Higasi [1]. Davies and Edwards [3] also found a similar relationship between ΔH_E and ΔS_E for polar molecules of various sizes and shapes of the types: camphor, anthrone, cholest-4-ene-3-one, tetracyclone, and β-naphthol. This linear dependence between ΔH_E and ΔS_E may be explained qualitatively if the activation energy is assumed to be largely needed to displace adjacent solvent molecules. Thus, the larger the energy required for ΔH_E the greater will be the local reorganizational entropy.

Dielectric relaxation time, τ, and the enthalpy of activation have also been related to molecular

rotational volume, the viscosity of the medium in which the process is occurring, and to the position of the dipole moment within the solute molecule.

The dependence of τ on molecular volume originates from a modification [5] of the Debye dielectric theory for spherical molecules [4], by Perrin and Fischer. The latter author proposed the following equation to describe the behavior of ellipsoidal molecules having semi-axes a, b, and c;

$$\tau = \frac{4\pi\ abc\ \eta^* f}{3kT} \qquad \text{IV-1}$$

where the volume of the ellipsoid is

$v = 4\pi abc/3$ and

η^* is the microscopic viscosity coefficient

f is a molecular structure factor

k is the Boltzmann's constant

and T is the temperature in degrees Kelvin

While this relationship is expected to apply to molecules

of similar size and shape, since η^* and f would be roughly constant [5], it has been found to be inadequate in describing polar molecular behavior even where both solute and solvent molecules are of similar size [6]. One possible reason for the divergence of observed relaxation times and those calculated from the Fischer equation IV-1 is the fact that the original Debye theory does not take into account the moment of inertia of the solute molecule [7,8]. In fact one factor, η^*, has never been determined convincingly in a fashion relevant to the applied equation. This viscosity term, depending upon the manner in which it is determined, may vary considerable. One such example is the highly viscous media Nujol. Depending upon the temperature at which the viscosity of Nujol solutions are measured, quite a range of viscosities will be observed. These values for η do not, however, necessarily represent the viscosity observed by solute molecules contained within the solution. This might be summed up by a comparison of the terms micro- and macroscopic viscosity. To date, researchers have at best been able to speculate on the extent to which surrounding solvent molecules influence the molecular and intramolecular behavior of solute molecules within the

solution [9,10]. Hence, any relationship between currently measurable viscosity data and the actual viscosity experienced by the solute molecule (microviscosity) is at best speculative.

Other workers have related size, shape, and direction of dipole moment to observed relaxation time. Crossley and Walker [11] studied three non-spherical rigid molecules in cyclohexane solutions at 323 K. While these solute molecules, quinoline, isoquinoline, and phthalazine, are of almost identical size and shape, the direction of their dipole moments varies. The interesting observation here is that within experimental limits of accuracy, there was no detectable variation in relaxation time for these molecules.

DiCarlo and Smyth [12] measured 4-iodobiphenyl and 2-iodobiphenyl in Nujol at 293 K and reported values of enthalpies of activation to be 31.8 and 25.9 kJ mol^{-1}, respectively. A six-fold increase in relaxation time was observed for the 4-iodobiphenyl over the 2-iodobiphenyl. This may be readily explained in view of the dipole moment in the former case lying along the long axis while in

the latter case it is skewed towards the same axis. Thus, the value of 31.8 kJ mol^{-1} most probably represents relaxation through a tumbling motion of the molecule about the short axis, resulting in a greater volume being swept out. In the case of 2-iodobiphenyl, relaxation must occur predominatly by rotation about the long axis. It is worth noting that, in the same medium, the value of 31.8 kJ mol^{-1} for the enthalpy of activation for 4-iodobiphenyl is smaller than the observed value of 37.6 kJ mol^{-1} for 4-bromobiphenyl.

Hassell [13] has studied some aromatic halide solutions of p-xylene at 288 K. He reported enthalpies of activation for the fluoro-, chloro-, bromo-, and iodobenzene series to be 5.9, 6.7, 8.4, and 9.2 kJ mol^{-1}, respectively. The indication here is that with increase in molecular size, there is a slight increase in ΔH_E. Both Hassell [13] and Cooke [14], however, found reasonable correlation between activation energy (kJ mol^{-1}) and volume swept out by the molecule for dilute solutions of mono-halobenzenes, ortho- and meta- di-halobenzenes, o-dibenzenes, m-dibenzenes, and naphthalenes in p-xylene.

As dielectric studies continued, increasingly

viscous systems were chosen to determine what effect, if any, highly viscous solvents would have on dielectric behavior [15,16]. Molecules were examined as solutions in Nujol/benzene and Nujol/n-heptane, the viscosity of which had been varied over the range of pure hydrocarbon to pure Nujol. The data showed that for most small, regularly-shaped molecules, little change in enthalpies of activation resulted when the viscosity of the sample solution was varied. This led investigators to believe that while the macroscopic viscosity of the system might be quite high, the microscopic or apparent viscosity of the solution as experienced by the relaxing molecule might, in fact, be quite low [9].

To examine further the effects of solvent on the relaxation characteristics of a molecule, macromolecular glass-forming systems have been used to trap molecules more tightly. One such glass-forming system is polystyrene. Khwaja [17] studied a series of rigid dipolar molecules belonging to the same family (i.e. the dipole moment lying along the longest axis). These measurements in polystyrene were carried out with a view to establishing a relationship between increasing molecular size and such parameters

as (1) the enthalpies and entropies of activation, (2) the enthalpies of activation and volume needed for re-orientation of the solute molecule, and (3) the dependence of molecular relaxation time on moments of inertia. The molecules studied were largely from the halo-substituted benzenes and toluenes.

One of Khwaja's aims was "to gain knowledge on the relaxation of a series of rigid molecules in such a matrix", i.e. one of extreme viscosity [18].

Recent studies of molecular glass forming systems have indicated an even more pronounced solvent effect on molecular reorientation. One such system, consisting of solutions of ortho-terphenyl as the solvent, has been studied over a wide temperature range, including measurements made in the region above its melting point, 328 K, [9,19] below its melting point as a super-cooled liquid [20,21,22], and, more recently, below its glass transition temperature, T_g, as a molecular glass [23].

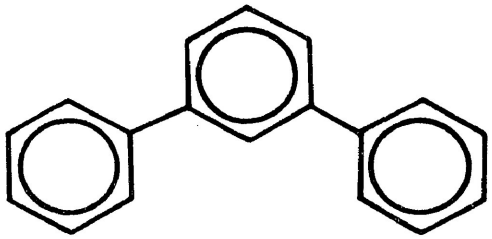
In this chapter, the results of a careful study of twelve key rigid molecules, chosen for their

increasing size, are presented so as to increase the understanding of molecular motion within this system. Further to this, correlations are presented which describe interesting media effects previously unreported.

The methods used to evaluate relaxation and activation parameters have been described previously (Chapter II).

All rigid molecules were commercially prepared and used without further purification. The structure of all rigid molecules studied in this section are given in Figure IV-1.

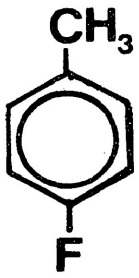
The solvent used in these studies, o-terphenyl, was commercially prepared by Polyscience Inc., and was used throughout without further purification. Tanδ vs T(K) curves were checked to see if there any difference between the various lots of o-terphenyl. None was observed.



a

b

c



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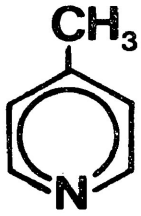

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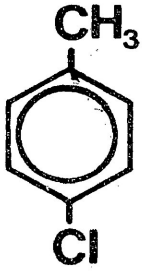
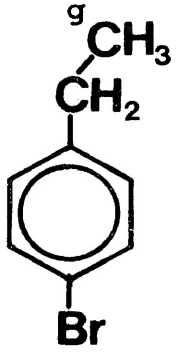


f

g

h

i



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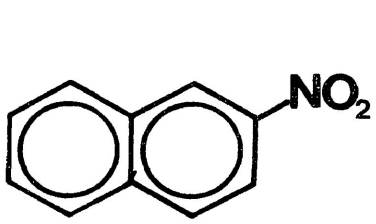

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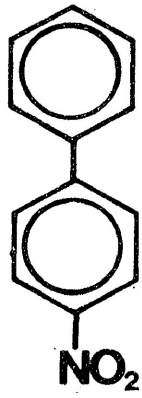

l

Figure IV-1

a	o-terphenyl	g	benzonitrile
b	pyridine	h	benzotrichloride
c	fluorobenzene	i	p-bromotoluene
d	p-fluorotoluene	j	p-bromoethylbenzene
e	γ-picoline	k	β-nitronaphthalene
f	p-chlorotoluene	l	p-nitrobiphenyl

EXPERIMENTAL RESULTS

The dielectric measurements of pure o-terphenyl, from liquid nitrogen temperature up to the glass transition temperature (T_g), have been made in the frequency range of 10^2 to 10^5 Hz and are presented here to establish clearly the characteristics of this molecular glass-forming solvent. Figures IV-2, IV-3, and IV-4 show plots of tanδ vs T, ε" vs logf and log($T\tau$) vs 1/T (K^{-1}) for the dielectric behavior observed in pure o-terphenyl.

Similarly, measurements were made over the same frequency and temperature ranges on the following molecules either as the pure solvent (glassy o-terphenyl) or as dilute solutions in o-terphenyl: pure o-terphenyl, pyridine, fluorobenzene, γ-picoline, p-fluorotoluene, benzonitrile, benzotrichloride, p-chlorotoluene, p-nitrotoluene, p-bromotoluene, p-bromoethylbenzene, β-nitronaphthalene, and 4-nitrobiphenyl.

Certain of these molecules, the absorption processes of which were outside the useful range for o-terphenyl, have also been studied. Table IV-1 shows

TABLE IV-1 RIGID MOLECULES STUDIED IN GLASSY o-TERPHENYL (Conc. by weight/weight <8%)

Molecule	T(K)	$\Delta\log f_{max}$	$\bar{\beta}$	τ(s) 100 K	τ(s) 150 K	τ(s) 200 K	ΔG_E (kJ mol^{-1}) 100 K	ΔG_E (kJ mol^{-1}) 150 K	ΔG_E (kJ mol^{-1}) 200 K	ΔH_E (kJ mol^{-1})	ΔS_E (J/K mol)
GOTP	267-280	2.13-4.64	0.56	-	6.0×10^{31}	2.5×10^{11}	162	127	92	233 ±23	703± 83
pyridine	79-97	2.01-3.20	0.18	3.0×10^{-11}	2.5×10^{-8}	2.0×10^{-9}	13.0	14.0	15.1	11 ±3	-20± 10
fluorobenzene	79-100	2.63-4.50	0.30	4.3×10^{-6}	2.1×10^{-8}	1.3×10^{-9}	13.0	14.0	14.0	12 ±3	-10± 20
γ-picoline	117-143	2.65-4.29	0.22	3.7×10^{-3}	4.5×10^{-6}	1.5×10^{-7}	18.9	20.5	22.2	16 ±3	-33±-26
p-fluorotoluene	138-185	2.79-4.30	0.20	4.1×10^{-1}	2.2×10^{-4}	4.8×10^{-6}	23.1	25.0	28.2	18 ±3	-51± 21
benzonitrile	179-197	2.85-3.60	0.19	1.3×10^{3}	1.1×10^{-2}	2.9×10^{-5}	29.5	30.2	30.9	28 ±3	-14±-15
p-chloro-toluene	204-241	2.11-3.21	0.20	1.8×10^{5}	2.0×10^{-3}	4.0×10^{-6}	33.2	34.3	34.0	29 ±4	-26± 20
benzyl-trichloro-ride	200-226	2.80-4.18	0.20	7.0×10^{-1}	2.6×10^{-1}	1.4×10^{-4}	34.8	34.2	33.6	36 ±5	12± 9

TABLE IV-2

Molecule	$\bar{V}(\text{Å}^3)$	Dielectric Observation
p-Bromotoluene	350	There was no sign of molecular contribution to that of the tanδ versus T(K) for pure glassy o-terphenyl although the apparent T_g for these systems was somewhat lowered perhaps owing to some plasticizing effect of the solute.
p-Bromoethyl-benzene	365	
p-nitrotoluene	377	These molecules showed general increase in tanδ with increase in temperature to about the expected T_g at which point the tanδ values increased dramatically characteristic of the phase change.
β-nitronaphthalene	365 [24]	
4-nitrobiphenyl	620	
		In the case of p-nitrotoluene, full frequency studies at spot temperatures were carried out to see how dielectric loss in this molecule varied with frequency at a fixed temperature. The indication is that the process is at a temperature above the glass transition temperature.
		The remaining two compounds showed a marked increase in tanδ with increasing temperature. They were not further studied.

NB: Tanδ versus T(K) curves are taken at fixed frequency and may be assumed to have been studied at 1 kHz unless otherwise indicated.

TABLE IV-3 EYRING PARAMETERS AND RELAXATION TIMES FOR SOME RIGID MOLECULES

Molecule	pyridine[a]	fluoro-benzene[b]	γ-pico-line[b]	p-fluoro toluene[b]	benzo-nitrile[b]	p-chloro-toluene[b]	benzyl-tri-chloride[b]	p-bromo-ethyl-benzene[b]
Volume $\AA^3$	185	217	263	261	295	321	336	350
ΔH^* (kJ mol^{-1})	11	12	16	18	27	29	36	/
ΔH^{**} (kJ mol^{-1})	3	9	14	26	22	26	20	38
$\Delta G^*_{150\ K}$ (kJ mol^{-1})	14	15	22	28	31	26	34	/
$\Delta G^{**}_{150\ K}$ (kJ mol^{-1})	N/A	13	18	21	25	28	26	36

*denotes measurements made as weight/weight solutions of <8% solute in glassy o-terphenyl

**denotes measurements made as weight/weight solutions of <8% solute in atactic polystyrene

N.B. The Eyring parameters quoted in Tables IV-1 and -3 are not necessarily accurate to the values quoted but are valid for comparative purposes. The ΔG and τ values will be the most accurate within the experimental temperature ranges studied.

Polystyrene results from: a, [28]
b, [17]

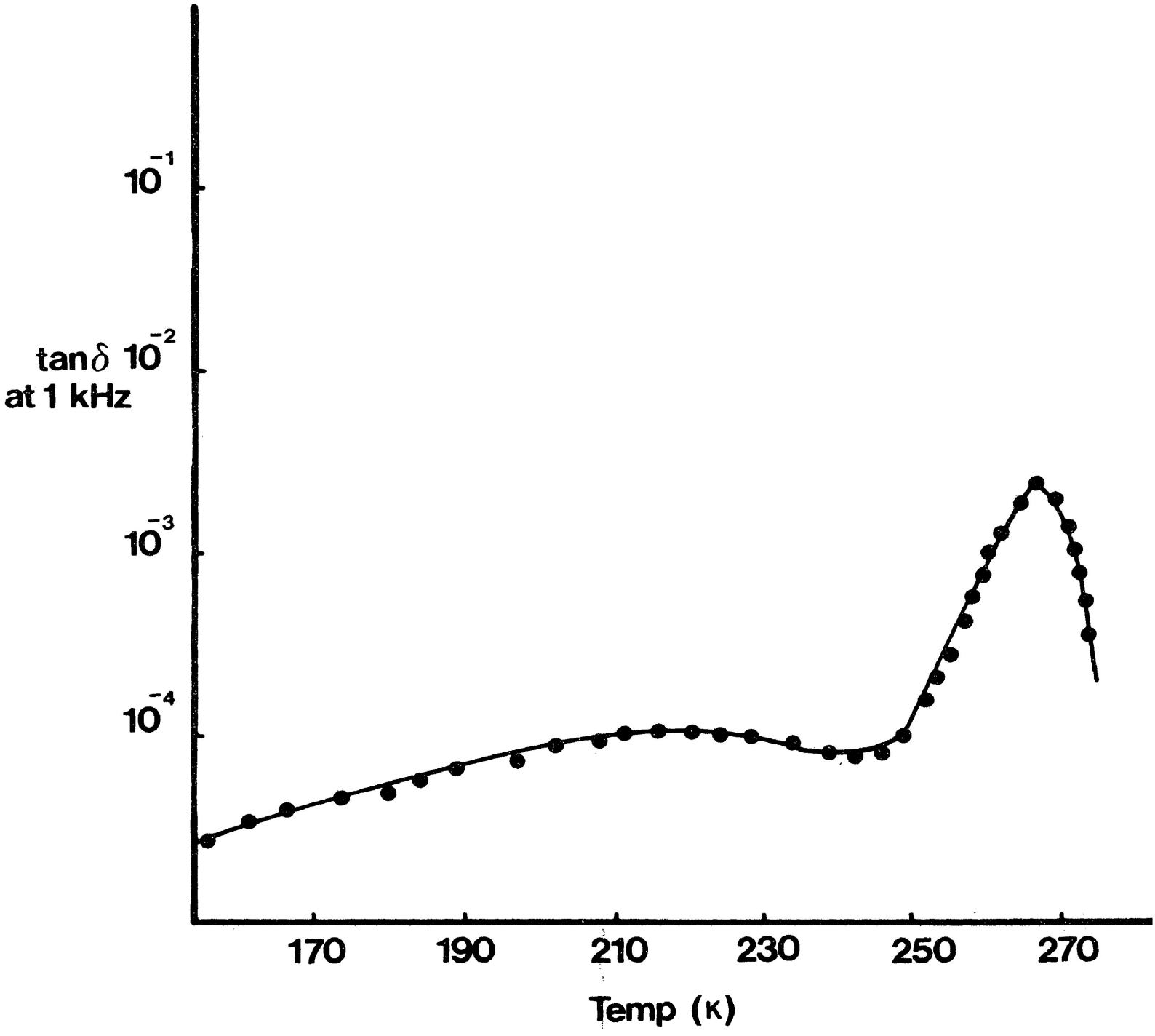

Figure IV-2 Plot of tanδ versus temperature (K) for glassy o-terphenyl at 1 KHz.

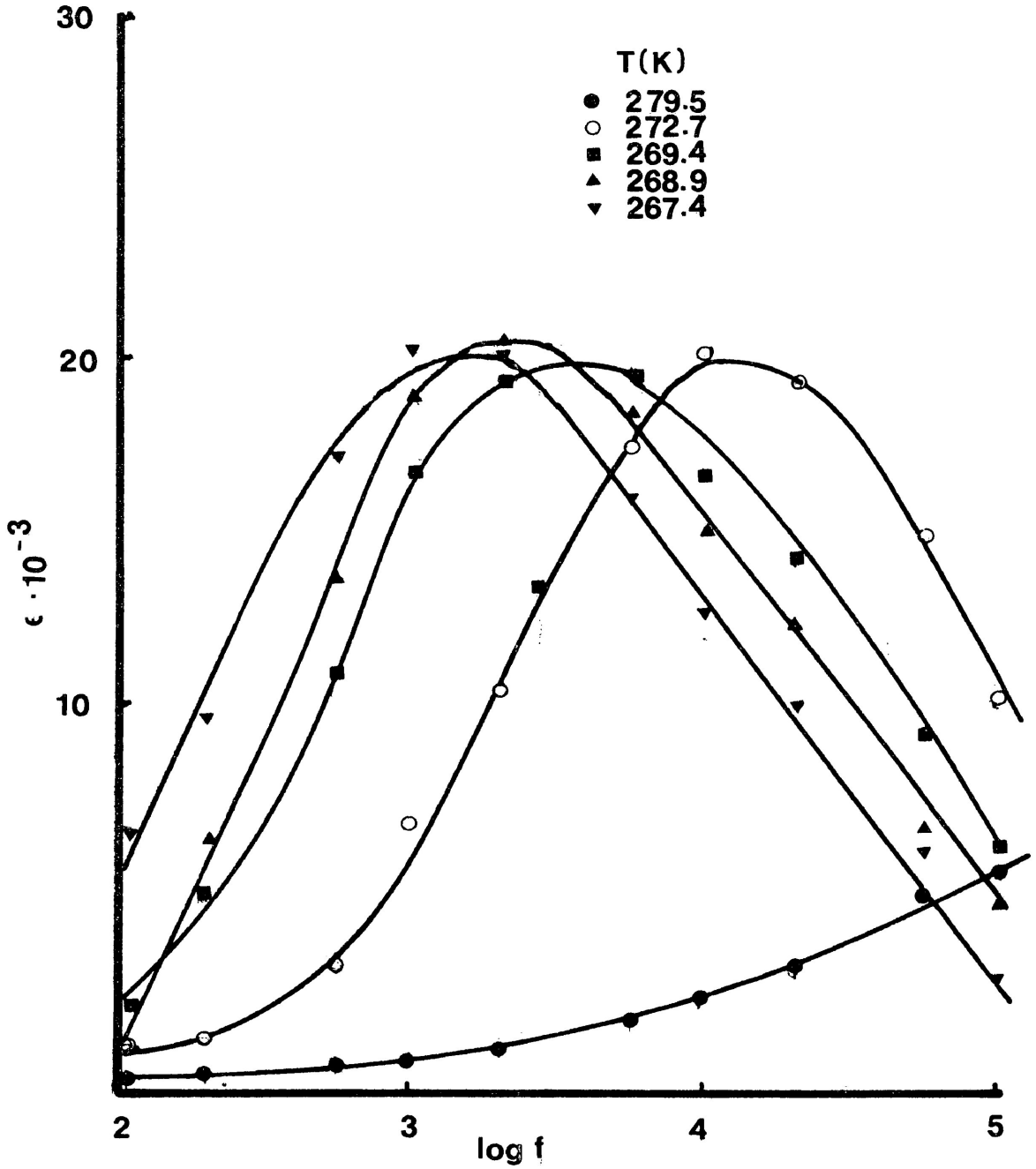

Figure IV-3 Loss versus Log frequency for pure glassy o-terphenyl

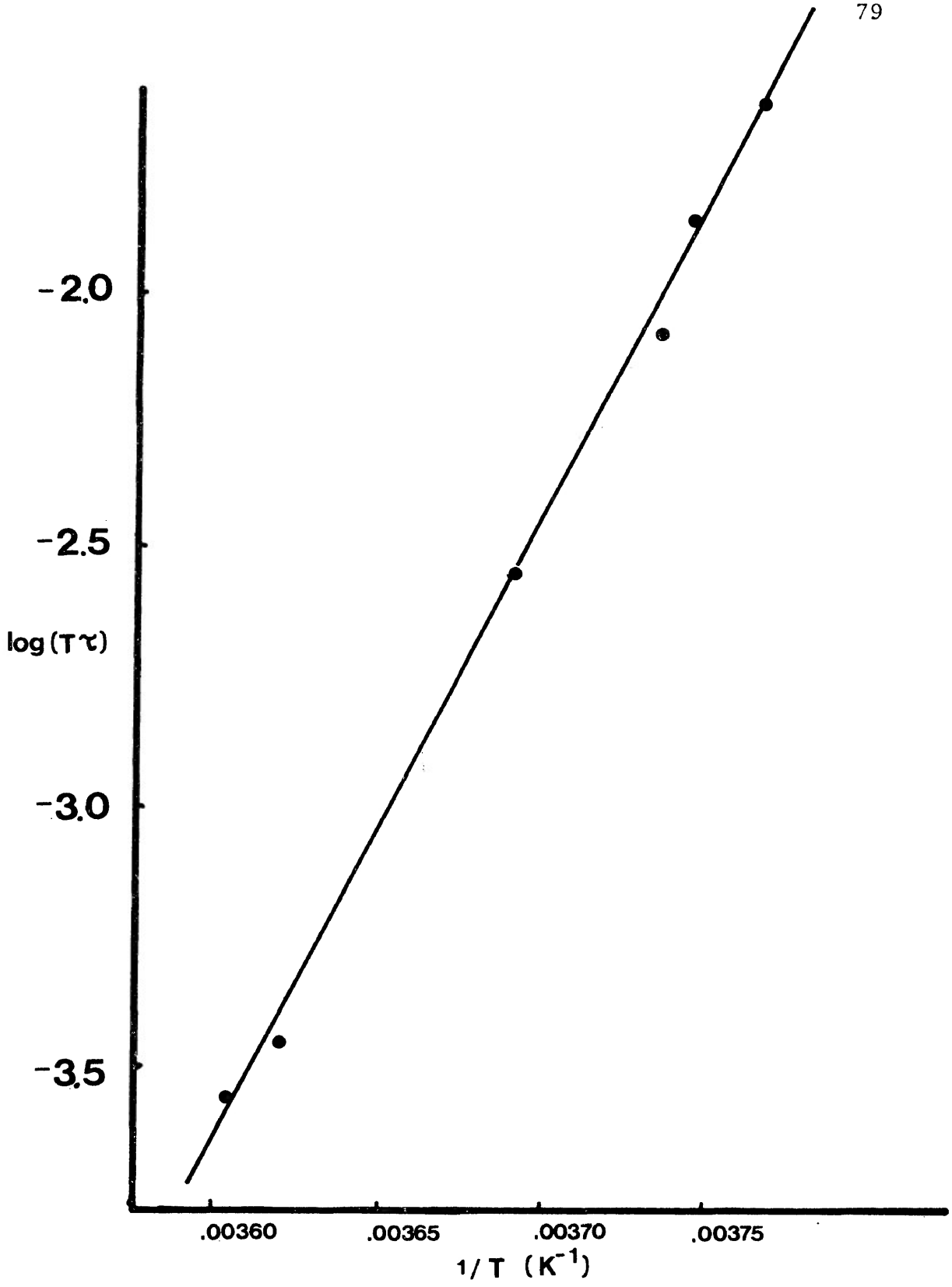

Figure IV-4 Eyring plot of Log (Tδ) versus 1/T (K^{-1}) for glassy o-terphenyl.

results for pure o-terphenyl and the seven rigid molecules, whose cooperative and molecular absorption processes respectively, were observed. Table IV-2 presents the results obtained for all other rigid molecules studied by this author in glassy o-terphenyl. A secondary aspect of this study of rigid molecules in glassy o-terphenyl has afforded the author, when the molecule had also been studied in polystyrene, an opportunity to determine what, if any, Eyring parameter relationships exist between the two media.

In fact, four such relationships were found which relate enthalpies of activation, and free energies of activation for the rigid molecules studied to the two media, to themselves, and to the mean volume swept out in $\mathring{A}^3$ ($\bar{V}$). They follow as equations IV-1, 2, 3 and 4.

(1) ΔH_{GOTP} vs $\Delta H_{P.S.}$ $\Delta H_{P.S.} = 0.50 \Delta H_{GOTP} + 3.30$

Equation IV-1

(2) ΔG_{GOTP} vs $\Delta G_{P.S.}$ $\Delta G_{P.S.} = 0.71 \Delta G_{GOTP} + 3.71$

where Δ_{G_E} is taken at 150 K

Equation IV-2

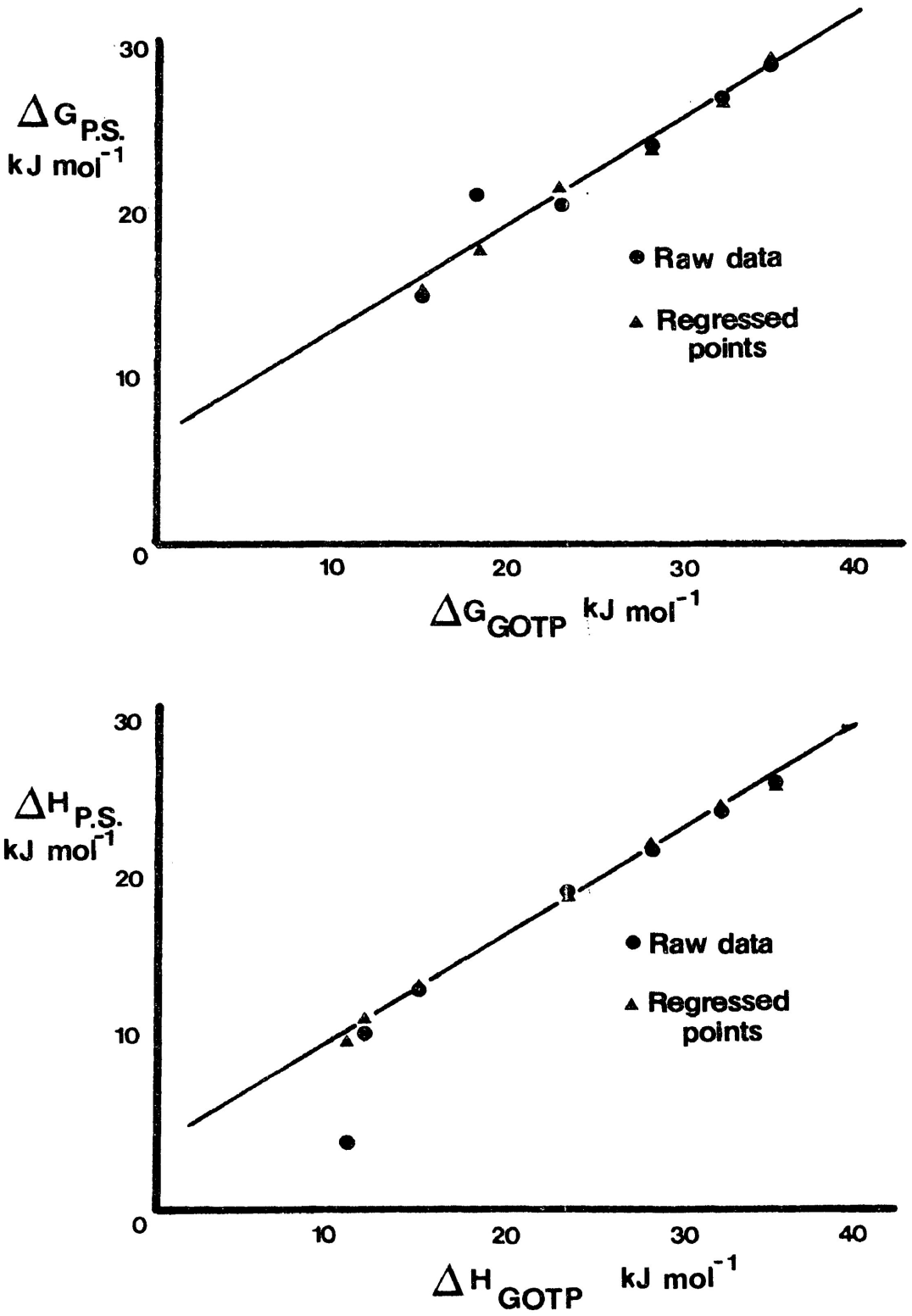

Figure IV-5 Plots of interrelation of enthalpies and free energies of activation in two solvent systems for molecules b through h (c.f. Figure IV-1

In a similar fashion relationships were drawn between the swept volume (Å^3) about the molecular centre of volume and ΔH_E and ΔG_E as follows:

(1) $\bar{V}$ vs $\Delta G_{150\ K}$ $\Delta G_{GOTP} = 0.16\ \bar{V}$ swept - 17.60

mean swept volume in Å^3

Equation IV - 3

and

(2) $\bar{V}_{\text{Å}^3}$ vs ΔH_E $\Delta H_{GOTP} = 0.21\ \bar{V}$ swept - 36.00

Equation IV-4

NOTE: Volumes of molecules as cited above are taken from [17] and/or were determined using Courtauld models.

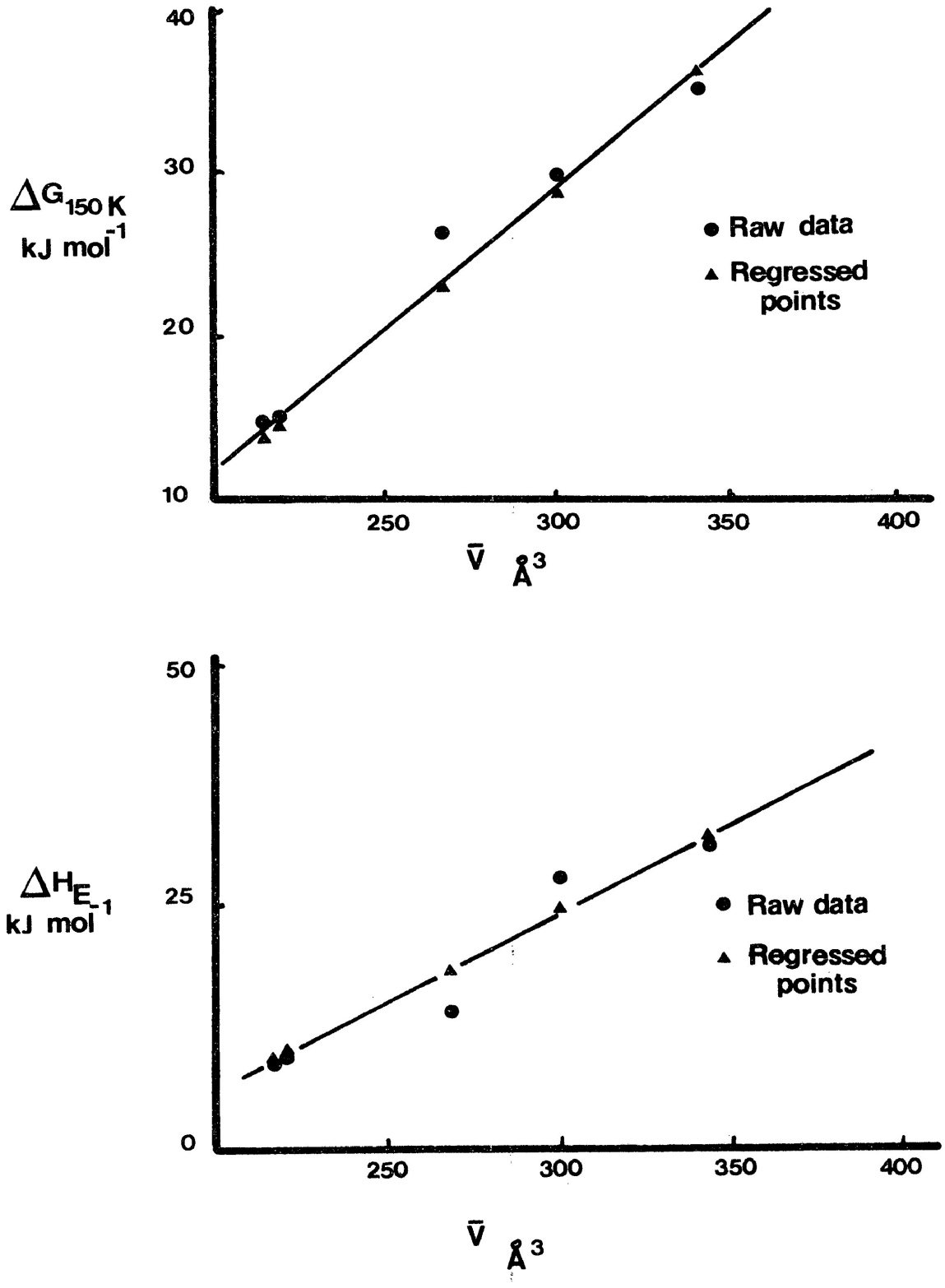

Figure IV-6 Plots of free energy of activation and enthalpy of activation against volume swept. (molecules b through h c.f. Figure IV-1)

From Table IV-2, those molecules demonstrating no relaxation process over the temperature/frequency range available are given. Each, in fact, has an average molecular volume swept out, $\bar{V}$, in excess of what appears to be the limiting value of $\sim$340 Å^3 for glassy o-terphenyl solutions.

The series of molecules studied, the results of which have been tabulated in Table IV-1, were particularly chosen to test the sensitivity of the medium to increases in molecular volume swept out during the relaxation process characteristic of that rigid molecule. Table IV-3, which follows, presents a comparison between molecular volume, in Å^3, swept out by a rigid molecule relaxing by rotation through its centre of volume for seven rigid molecules in the solvent glassy o-terphenyl and, for comparison, atactic polystyrene.

Most important to note is that those molecules showing no relaxation characteristics have estimated volume requirements in excess of 340 Å^3.

A number of representative tanδ vs temperature (K),

loss vs log frequency and Eyring plot figures is offered following this section and precede the references. These are typical of the results obtained for rigid molecules studied in glassy o-terphenyl.

DISCUSSION

In determining the suitability of a solvent for use in dielectric studies, a number of factors must be reviewed. Firstly, the solvent must be of relatively low loss over its useful range. It should be stable in the phase in which the measurements are being made and, of course, yield reproducible results. Solubility of solutes within the solvent is also important as concentration plays a significant role in determining the magnitude of the observed absorption. Finally, a clear understanding of the relative freedom of molecular motion should be assessed as accurately as possible from the experimental data. In this last regard, GOTP (glassy o-terphenyl) has been studied with rigid molecules of increasing size to help predict molecular contributions thought to be overlapping with intramolecular processes in flexible molecules and also to identify the molecular process when the molecular

and intramolecular processes have been separated. Thus, an absorption process observed in a flexible molecule, the size of which is such that any molecular absorption would be at a temperature well above or below the observed process, may reasonably be attributed to the relaxing group. To this end then, a useful correlation between observed ΔG_E in kJ mol^{-1} values and molecular size expressed in terms of $\AA^3$, swept out as the molecule rotates about its centre of volume, has been found.

Tay and Walker [24] found a linear relationship between the enthalpy of activation and the volume swept out by the molecule for certain halonaphthalenes dispersed in a polystyrene matrix. Later, Khwaja [17] set about to test this relationship for a wide range of rigid molecules including halobenzenes, p-halotoluenes, and p-halobiphenyls dispersed in a polystyrene matrix. All of these molecules have one thing in common: the dipole moment always lies along the longest axis. The following diagram illustrates the point. The molecular axes, x, y, and z, are in order of decreasing length. The molecular dipole lies along the x axis. Arrows about the y and z axes describe possible molecular rotations:

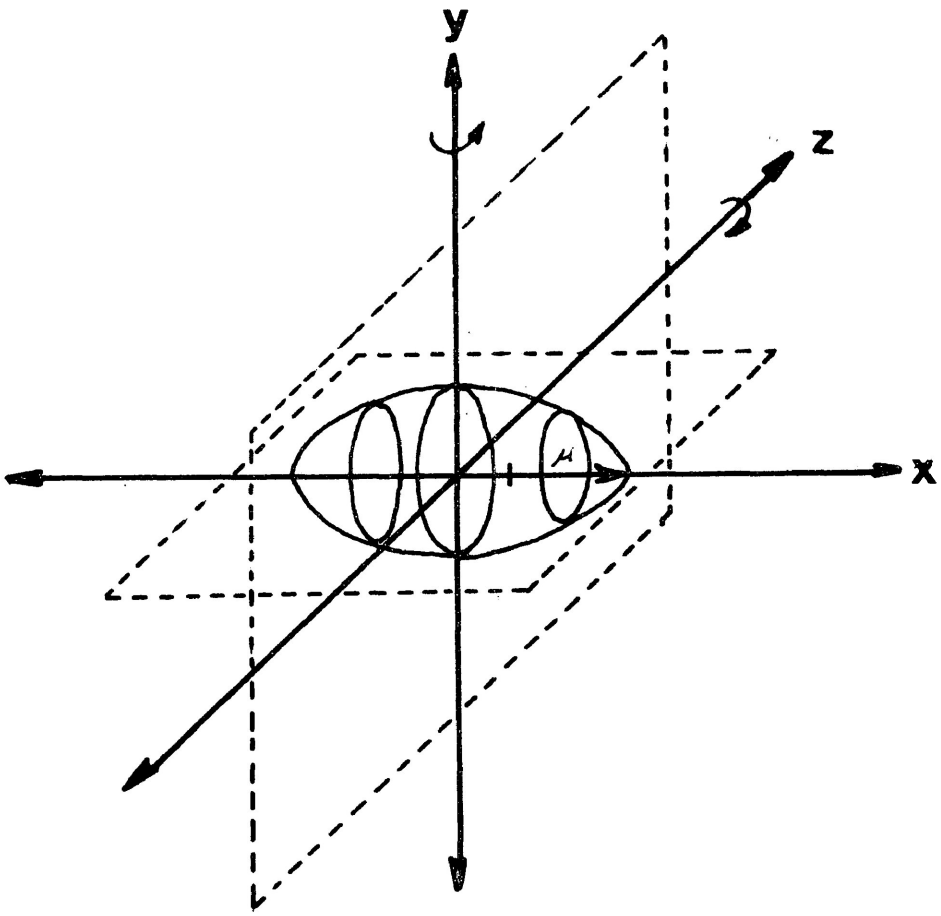

Figure IV-7 Elongated molecule, the dipole moment of which lies along the principal axis.

Inasmuch as the dipole lies along the long molecular axis, two extreme swept volumes may be expected. The first and largest results from rotation about the z axis. This rotation results in what may best be visualized as a tumbling motion. The other possibility is a rotation about the y axis. This planar rotation requires the displacement of adjacent solvent molecules. The point through which the x, y, and z axes pass is the centre

of mass. However, unlike the case of a gas, the rotation relating to the jostling motion molecules experience in the liquid state may well result in the molecule rotating about its centre of volume.

Since the centre of mass or volume, effective radii, and the length of the rotating species can readily be calculated or measured from molecular models [17], volumes swept out in each of the two possible rotational modes and the average of the two can be determined.

For rotation, either about the centre of mass or the centre of volume (x), the swept volume is composed of two half cylinders, the radii of which were taken to be the maximum lengths of the molecules in each direction from the point of rotation and the cylinder lengths to be the length of the molecule in the axis of rotation.

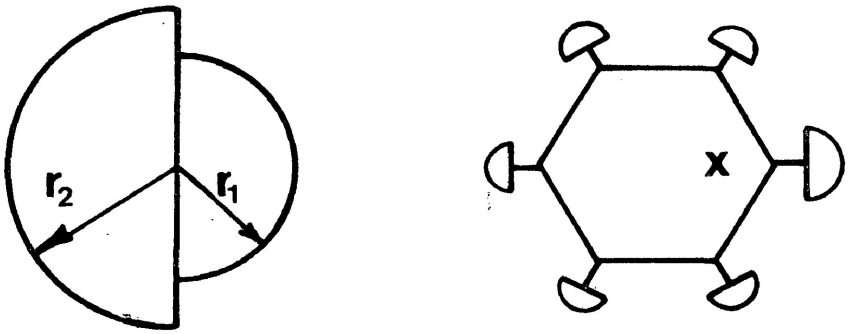

Figure IV-8 Models from shich the volume swept calculations were made.(this example represents fluorobenzene)

For fluorobenzene, molecular reorientation volumes swept out about the y axis are given in Tables IV-2 and IV-3 for the rigid molecules studied in GOTP.

Khwaja found reasonably linear correlations for ΔH_E (kJ mol^{-1}) and $\log\tau$ ($\tau_{200\ K}$) against the mean rotational volume ($\bar{V}_{mean}$) for rotations of certain rigid molecules studied in polystyrene about the centre of volume of these molecules.

Similar linear dependence of ΔH_E and ΔG_E against $\bar{V}_{swept}$ was observed in glassy o-terphenyl. The actual equations, IV-3 and -4, have been given in the experimental results section of this chapter.

Glassy o-Terphenyl as a Solvent

To address the first point, glassy o-terphenyl can readily be seen to be a low loss material in the temperature region below the glass transition temperature, Tg. (see Figure IV-2). At the Tg, reported by Crossley et al [23] to be ≃243 K, the rigid molecular glass begins

to move more freely and we observe, over the temperature region 267-280 K, an absorption process due to the cooperative motion of the o-terphenyl. This process, found to be above the T_g, has been termed the α-process.

The α-process in pure o-terphenyl has an enthalpy of activation of 233 kJ mol^{-1}, and an entropy value of 703 J K^{-1} mol^{-1}. The large ΔS_E implies considerable disorder as would be expected above the Tg. The enthalpy of activation, ΔH_E, is too large to be due to the motion of just one or even several molecules but is rather more likely a result of bulk reorganization of large molecular aggregates. This is also in keeping with the large positive entropy value of $\Delta S_E \simeq 700$ J K^{-1} mol^{-1}. The large distribution parameter 'β' of, on average, 0.6 implies a rather narrow range of relaxation times, tending toward Debye behavior. Figure IV-3 shows the reasonably symmetric ϵ" vs $\log_{10} f$ from which the Eyring parameters for this system have been calculated. Figure IV-4 is a plot of $\log_{10}(T\tau)$ against $1/T$ (K^{-1}).

A close examination of Figure IV-9 indicates four sites of major importance identified by the letters

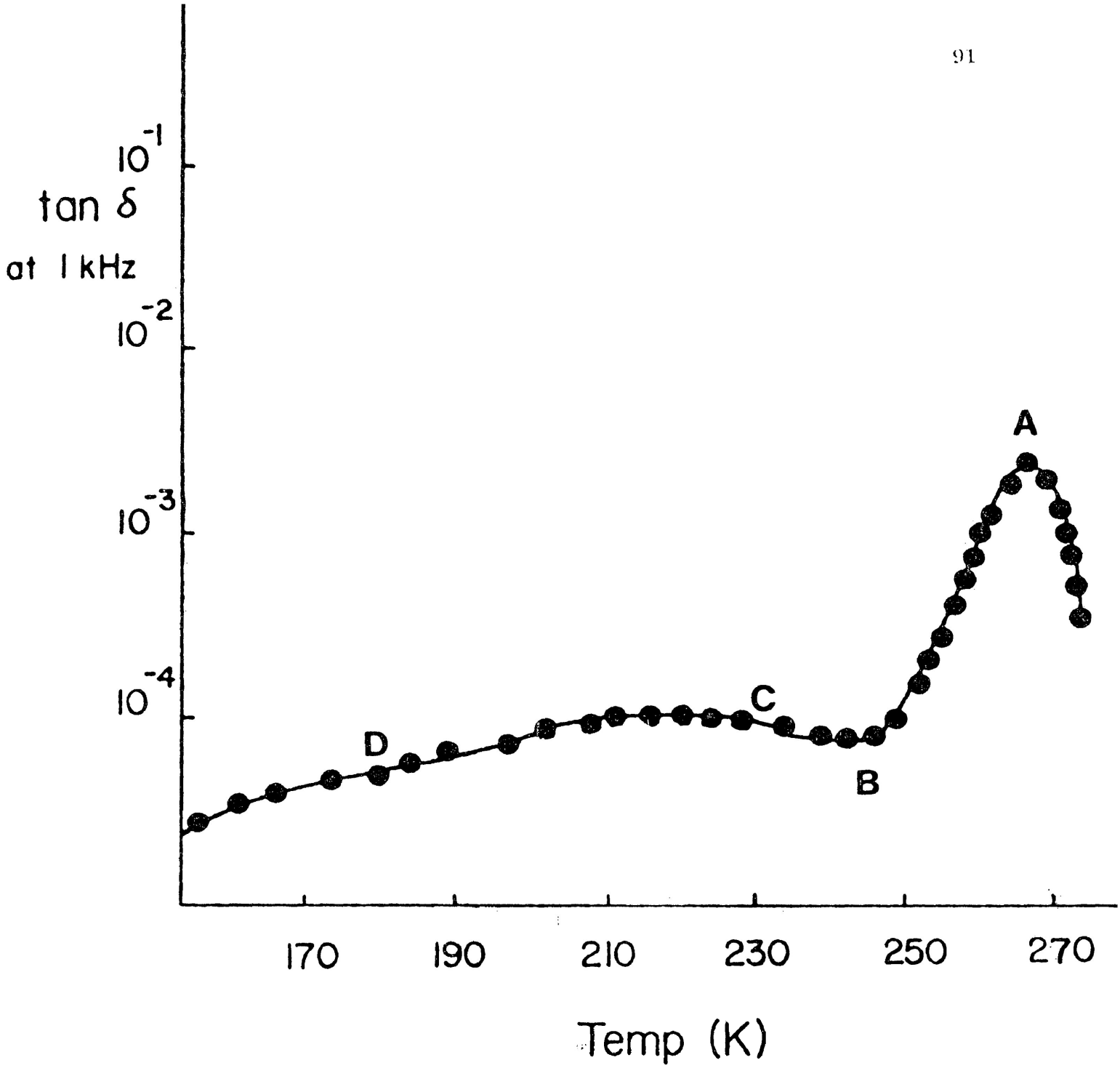

Figure IV-9 Selected points A through D for the the temperature scan of glassy o-terphenyl.

A through D. 'A' represents the point at which temperature (at a fixed frequency of 1 KHz) tanδ reaches its maximum. This is the region designated as the α-process in much of the literature [25,26]. 'B', the glass transition temperature, has also been referred to as the Tg, the temperature where bulk molecular reorganization begins. Between points D and C, the β process has been assigned.

The most important aspect of this curve is that in the region below the glass transition temperature, T_g, the tanδ value at 1 KHz reaches a maximum value of only $\sim 1 \times 10^{-4}$.

To summarize the preceding results, two important aspects of glassy o-terphenyl as a dielectric solvent have emerged. First, the region C-D may reasonably be considered the 'β' or lower temperature process associated with perhaps the relaxation of some aspect of the o-terphenyl system (β here not be be confused with the distribution parameter β).

The second point is that o-terphenyl is an essentially non-polar material. Its low $\tan\delta < 10^{-4}$, loss nature from liquid nitrogen temperature up to near the glass transition temperature of $\sim$343 K, contributes little to the observed loss and so, except perhaps for very low loss solutes (or solutes in very low concentrations), need not for the most part be considered.

Rigid Molecules Studied in Glassy o-Terphenyl

The smallest rigid molecule to be studied in glassy o-terphenyl was pyridine. The Eyring parameters determined for this molecule, studied at near liquid nitrogen temperature, are within experimental error, identical to those observed for fluorobenzene in the same media. On comparison of τ(s) and ΔG_E (kJ mol^{-1}) values at 150 K, we find that they are for pyridine and fluorobenzene, $\tau = 2.5 \times 10^{-8}$ s, $\Delta G_E = 14.0$ kJ mol^{-1}, and $\tau = 2.9 \times 10^{-8}$ s, $\Delta G_E = 14.2$ kJ mol^{-1}, respectively.

The next molecule to be studied was p-methylpyridine (γ-picoline). It certainly differs in mass from pyridine by an increase of ∿15 mass units. More significant is the greater volume swept out by the relaxation of this molecule. The molecular dipole, as in its fluoronated counterpart p-fluorotoluene, lies along the long molecular axis and so can relax by only two types of motion. The first, and least favoured from an energy point of view is through an end on end tumbling motion through the principal axis. This would clearly sweep out the largest volume of surrounding solvent while the less volume demanding motion, that of spinning in the plane of the phenyl ring, would seem more likely. Again, the Eyring parameters are, within experimental error, identical to each other (see Table IV-1). When the para substituent was changed to a larger, heavier halogen, namely chlorine, the position of the loss curves for p-chlorotoluene moved to higher temperatures, as would be expected. (T (K) 204-240 K, ΔH_E ≃29 kJ mol^{-1}, ΔS_E ≃-46 J K^{-1} mol^{-1}).

Benzonitrile, a mono-substituted benzene

having its molecular dipole moment coincident with its principal axis yielded and absorption process between 179-197 K with τ and ΔG_E at 150 K of 1.1×10^{-2} s and 30 kJ mol^{-1} respectively. The enthalpy of activation, ΔH_E, is approximately 28 kJ mol^{-1} having an associated entropy of activation, ΔS_E, of -14 J K^{-1} mol^{-1}. These values all agree well with later studies done by other workers in this laboratory [27].

p-Chlorotoluene was found to have an absorption process over the temperature region 204-230 K. The ΔH_E and ΔS_E values observed were 29 ±4 kJ mol^{-1} and -26 ±20 J K^{-1} mol^{-1}, respectively. The next molecule to be studied was benzotrichloride. This is the largets molecule studied which gave any indication of a molecular absorption process. This process was found between 200 and 226 K. It has a large ΔG_E and the longest relaxation time at 150 K of all the rigid molecules studied in glassy o-terphenyl by this author. They are 2.6×10^{-1} s and 34.2 kJ mol^{-1}, respectively. The enthalpy of activation is approximately 36 kJ mol^{-1} with a ΔS_E of 12 J K^{-1} mol^{-1}.

Molecules Showing No Molecular Relaxation

A molecule rather similar to p-bromotoluene is p-bromoethylbenzene. The principal molecular axis has remained the same relative to p-bromotoluene with the exception that the molecule is one methylene group longer. This molecule had been studied by this author several years earlier and, upon reproduction of the experiment using a more sophisticated coaxial cell, yielded the same results, namely no appreciable loss over the temperature and frequency range available. The estimated volume swept out by p-bromotoluene is $\sim$350 $\mathring{A}^3$. para-Bromoethylbenzene is slightly larger in that its length has been increased by one methylene group. The volume swept, $\overline{V}$, by this molecule is estimated to be just slightly larger, 365 $\mathring{A}^3$. It is in this light that the absence of absorption processes for these molecules is quite reasonable.

p-Bromoethylbenzene has been successfully studied in polystyrene, the results of which are presented in Table IV-3. In comparison with results obtained in glassy o-terphenyl, it is not surprising that with ΔH_E and $\Delta G_{E200\ K}$ of approximately 38 and 35 kJ mol^{-1}

respectively in polystyrene (24) the loss maxima over the frequency and temperature range studied were not observed. From the ΔH_E polystyrene vs ΔH_E GOTP, Figure IV-5, graph the ΔH_{GOTP} may be estimated to be 65.5 kJ mol^{-1} while from the ΔH_{GOTP} vs $\bar{V}_{(\text{Å}^3)}$ graph, Figure IV-5, the $\Delta G_{GOTP_{150\ K}}$ would be of the order of 38.4 kJ mol^{-1}.

Another molecule which has been studied successfully in polystyrene but failed to yield a detectable absorption process in the temperature/frequency range available in glassy o-terphenyl is 2-bromonaphthalene. While this molecule differs from the others in this study in that the dipole moment does not lie along the long molecule or principal axis, the negative results obtained in glassy o-terphenyl may suggest volume constraints being placed on its molecular motion worthy of further studies in molecular glass forming systems. Similarly, 4-nitro-biphenyl once again shows no dielectric activities in glassy o-terphenyl. This system had also been studied previously [19] by this author with similar results being obtained.

Examination of estimated $\bar{V}$ (Å^3) requirements for

these two molecules indicate that their molecular processes should be at temperatures above the glass transition for o-terphenyl.

While correlations between enthalpies and free energies of activation against mean volume swept were quite high (i.e. $r^2 \geq 0.9500$), attempts to compare the enthalpy of activation for these rigid molecules with the corresponding entropy values were not successful. This is most probably a consequence of the large error limits which often need to be placed on the latter term, sometimes as high as ±50% of the derived value, due to the long extrapolation to the Log(T_τ) axis from which the entropy factors are calculated.

One must also consider possible plasticizing effects of solute molecules on the glassy system and so in certain cases, the upper temperature limit of study becomes even lower (i.e. a lowering of the glass transition temperature, T_g, below that estimated by Crossley et al to be ≃243 K).

It would seem reasonable to suggest that, for molecules having dipole moments along the principal or long molecular axis and the requisite volume swept, the range of which is

between 216 $\mathring{A}^3$ and approximately 340 $\mathring{A}^3$, there will be likely some molecular relaxation process when studied in the medium glassy o-terphenyl in the temperature and frequency ranges previously stated.

Whether this will significantly affect the observed intramolecular barriers depends upon a number of factors which will be discussed in the following chapter.

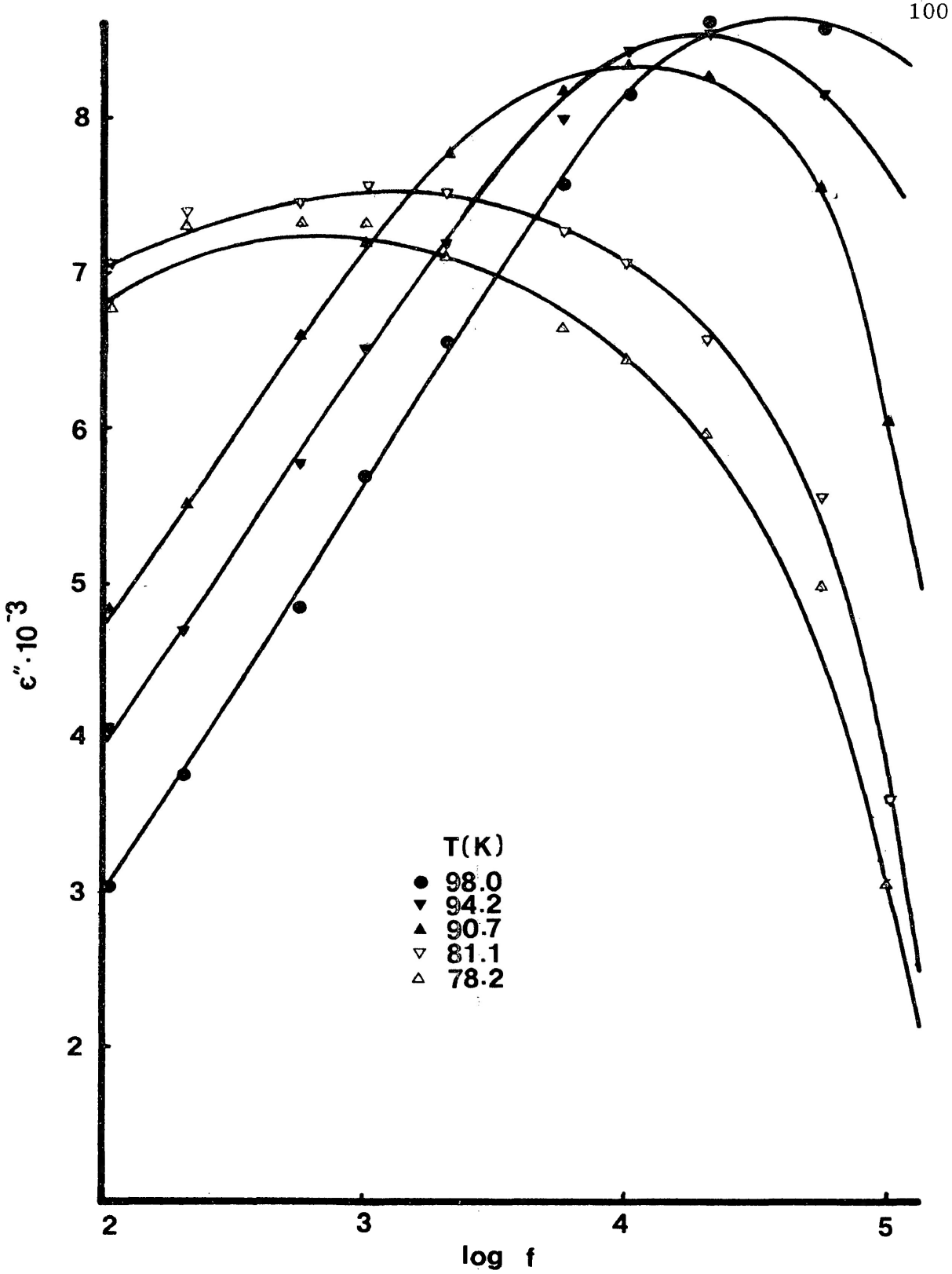

Figure IV-10 Plot of loss versus log frequency for fluorobenzene in glassy o-terphenyl, 5 percent by weight.

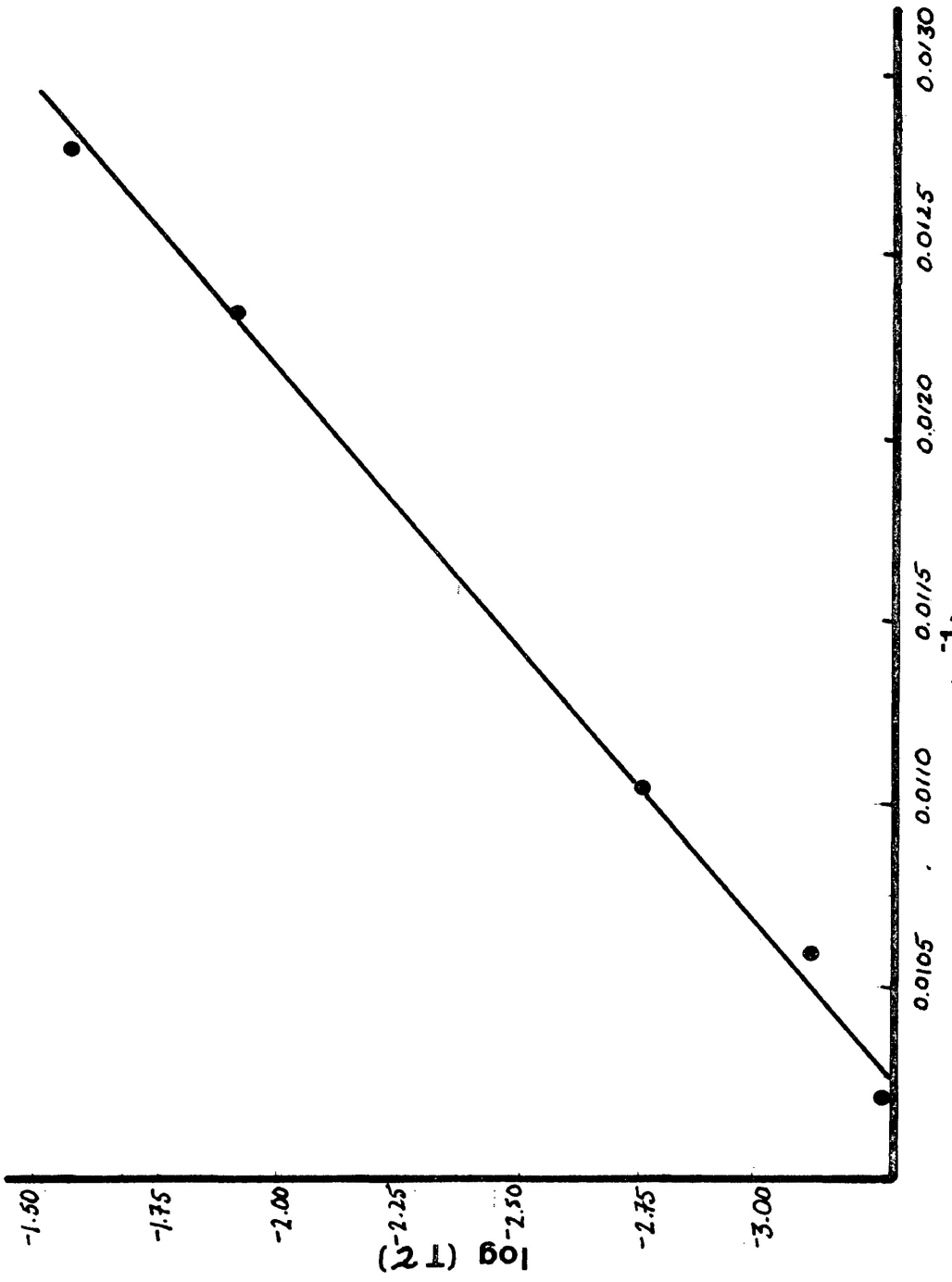

Figure IV-11 Eyring parameter for the preceding graph

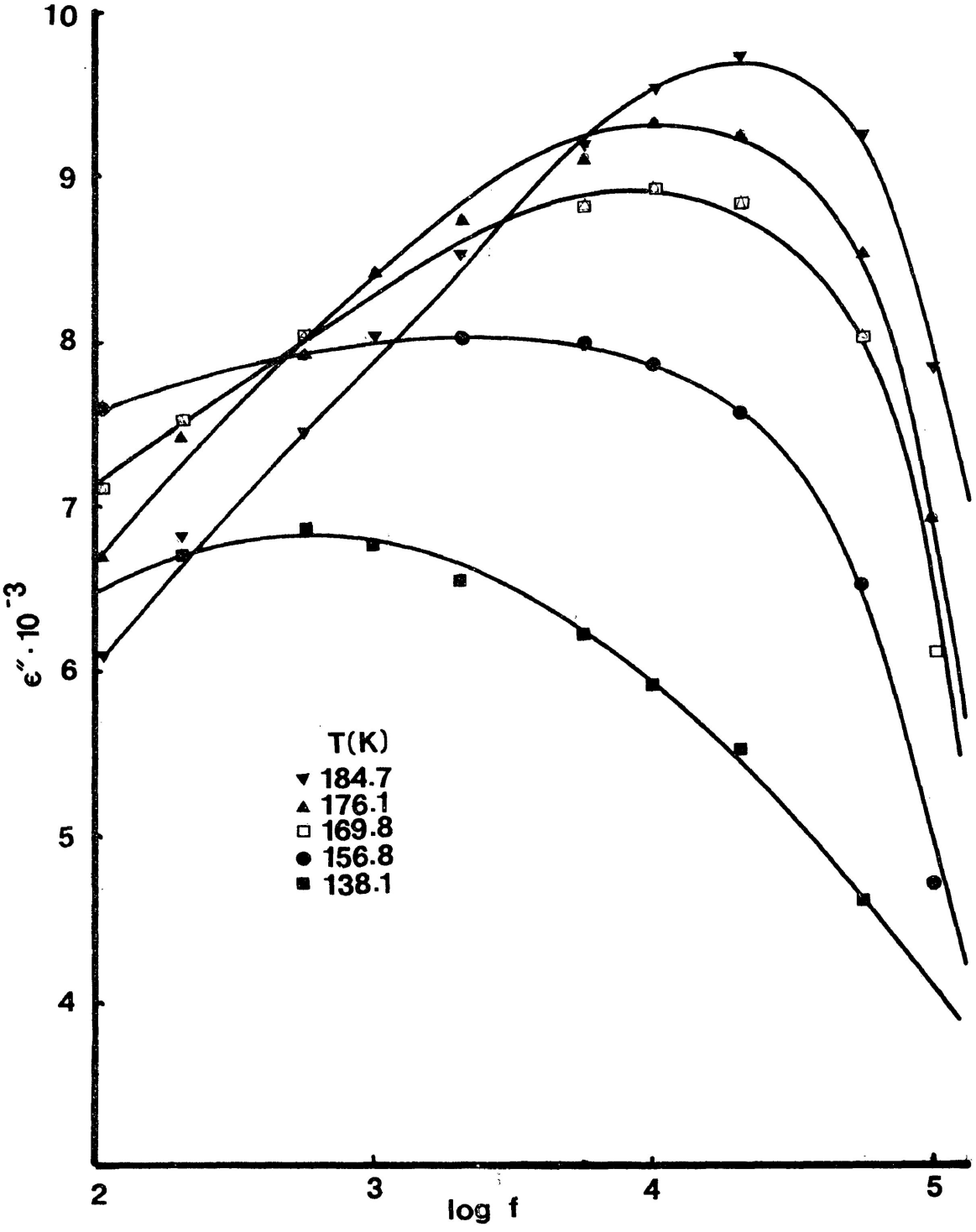

Figure IV-12 Plot of loss curves for p-fluorotoluene studied in glassy o-terphenyl, 5 percent by weight.

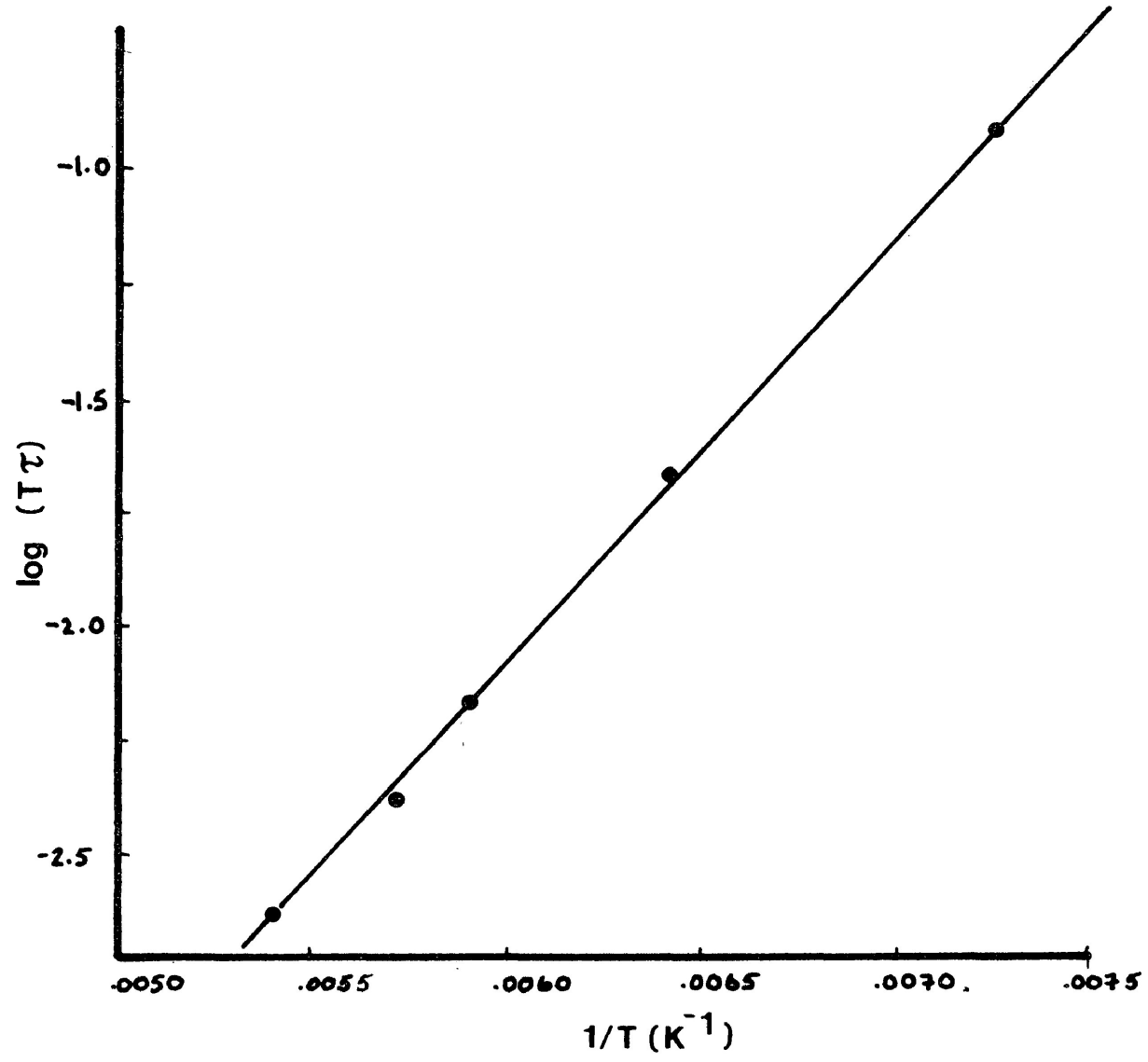

Figure IV-13 Eyring plot for the preceding graph.

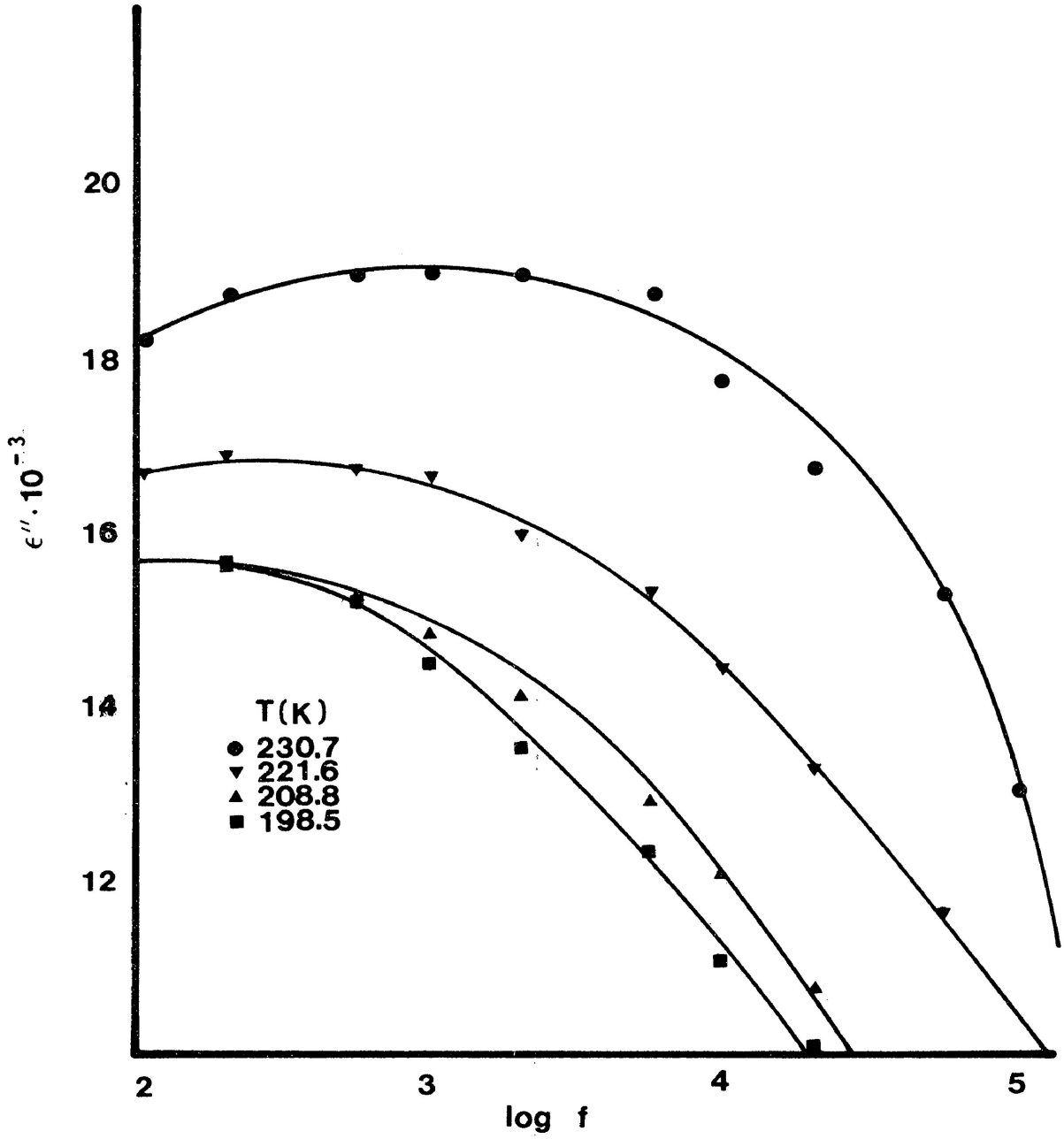

Figure IV-14 Plot of loss versus log frequency for p-chlorotoluene as studied as a 5 percent solution, by weight, in glassy o-terpheny.

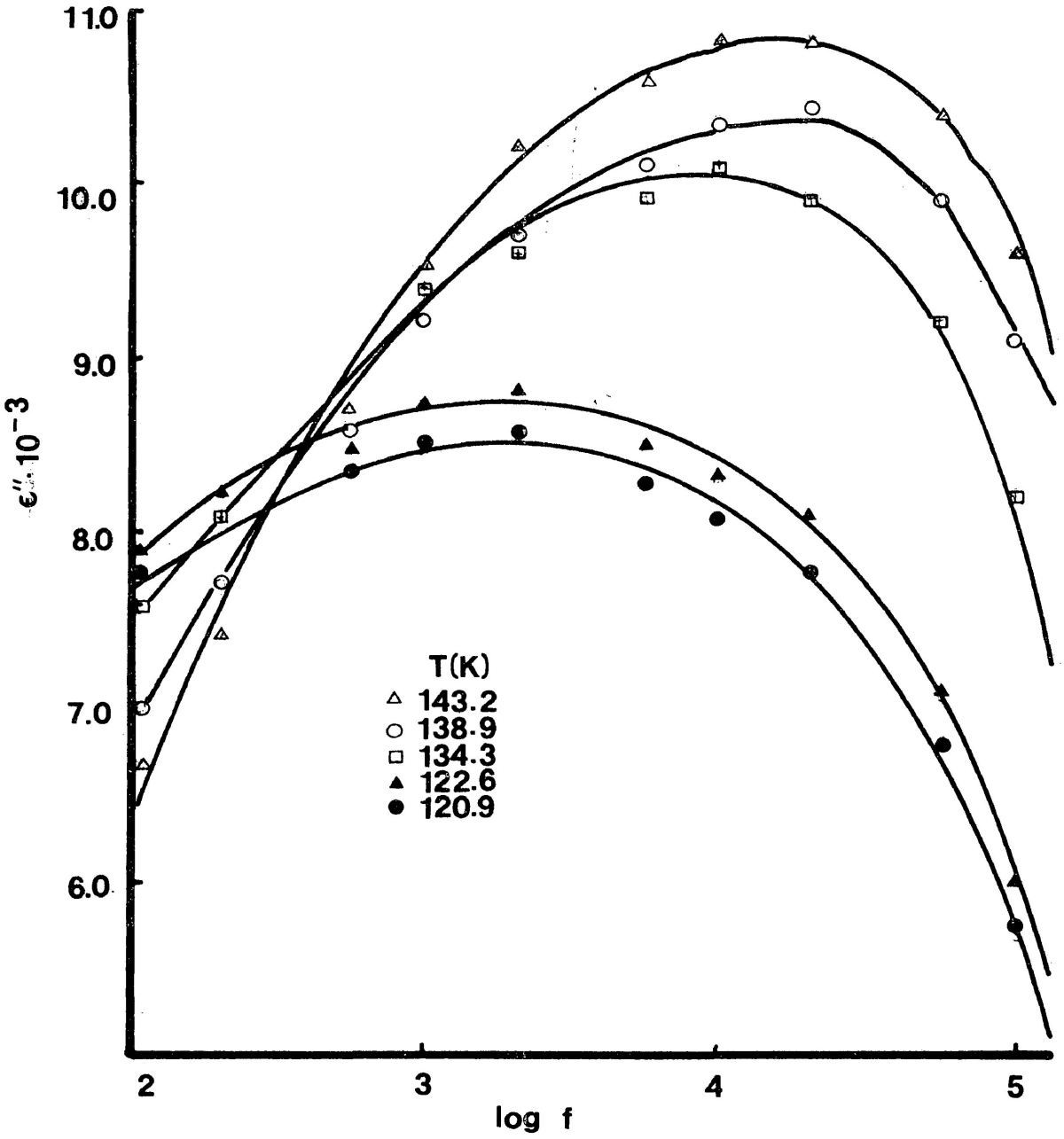

Figure IV-15 Plot of γ-picoline loss curves against log of the frequency as studied in glassy o-terphenyl, 5 percent by weight.

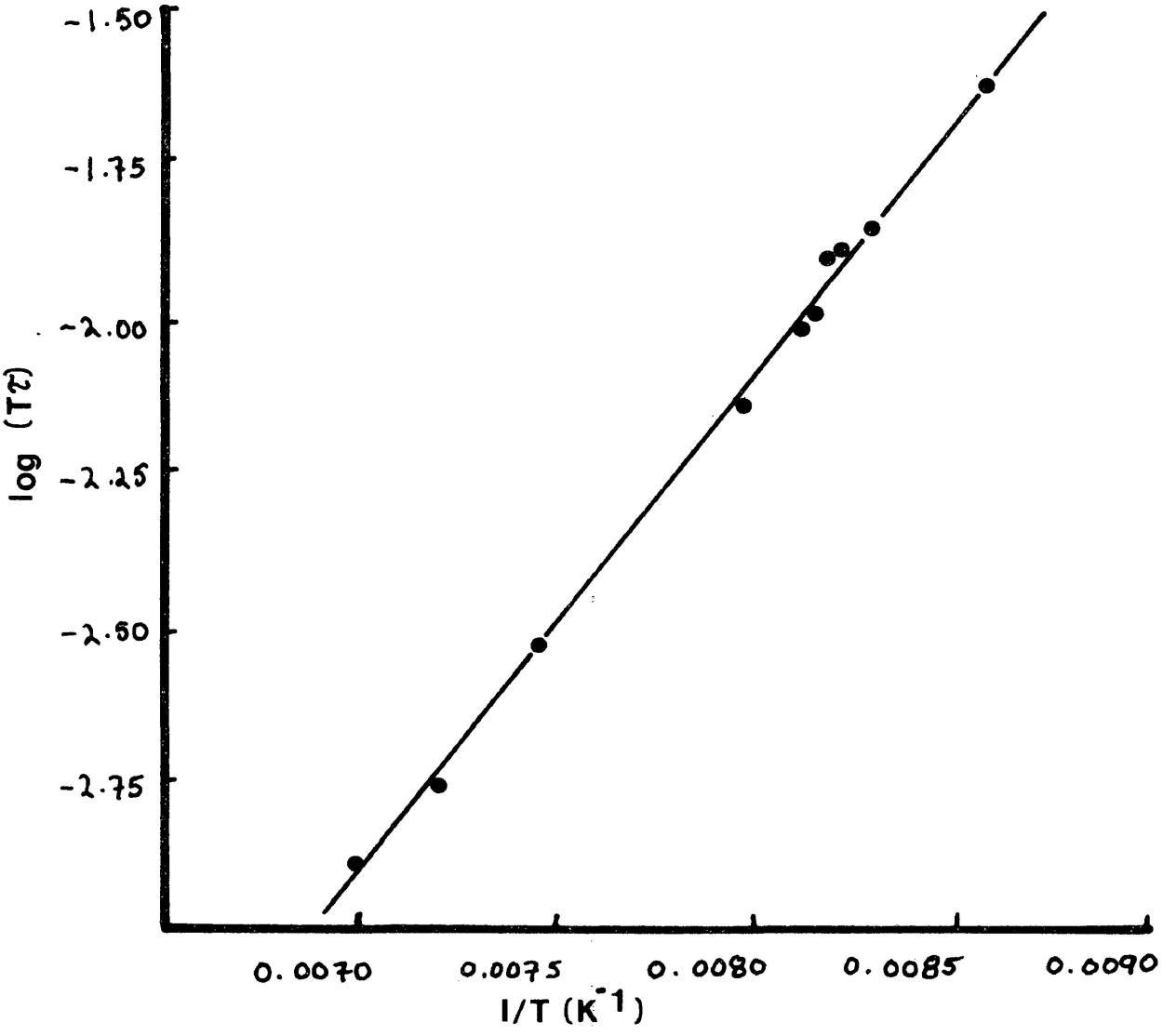

Figure IV-16 Eyring plot for preceding graph.

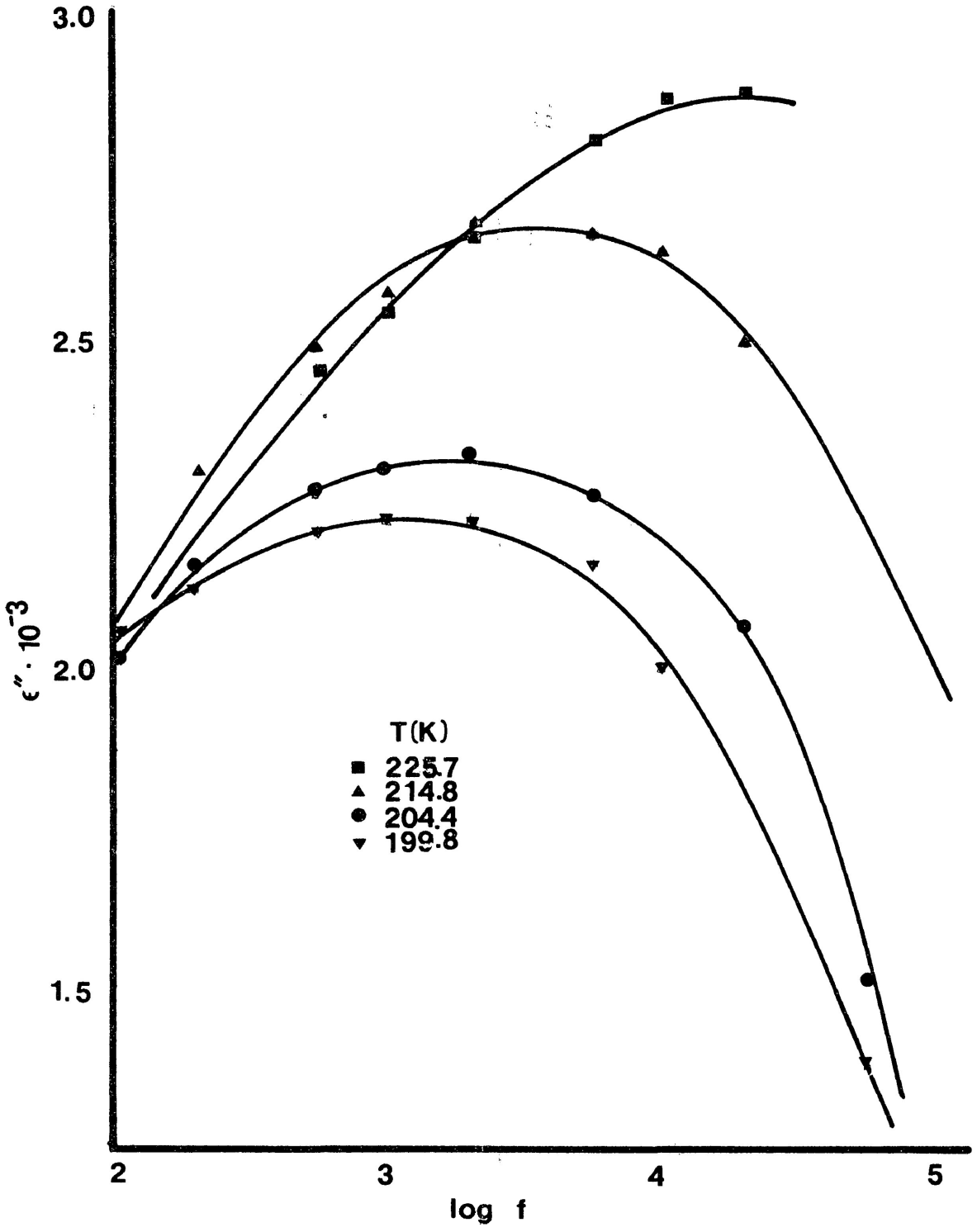

Figure IV-17 Loss curves for benzotrichloride, 5 percent by weight, as studied in glassy o-terphenyl.

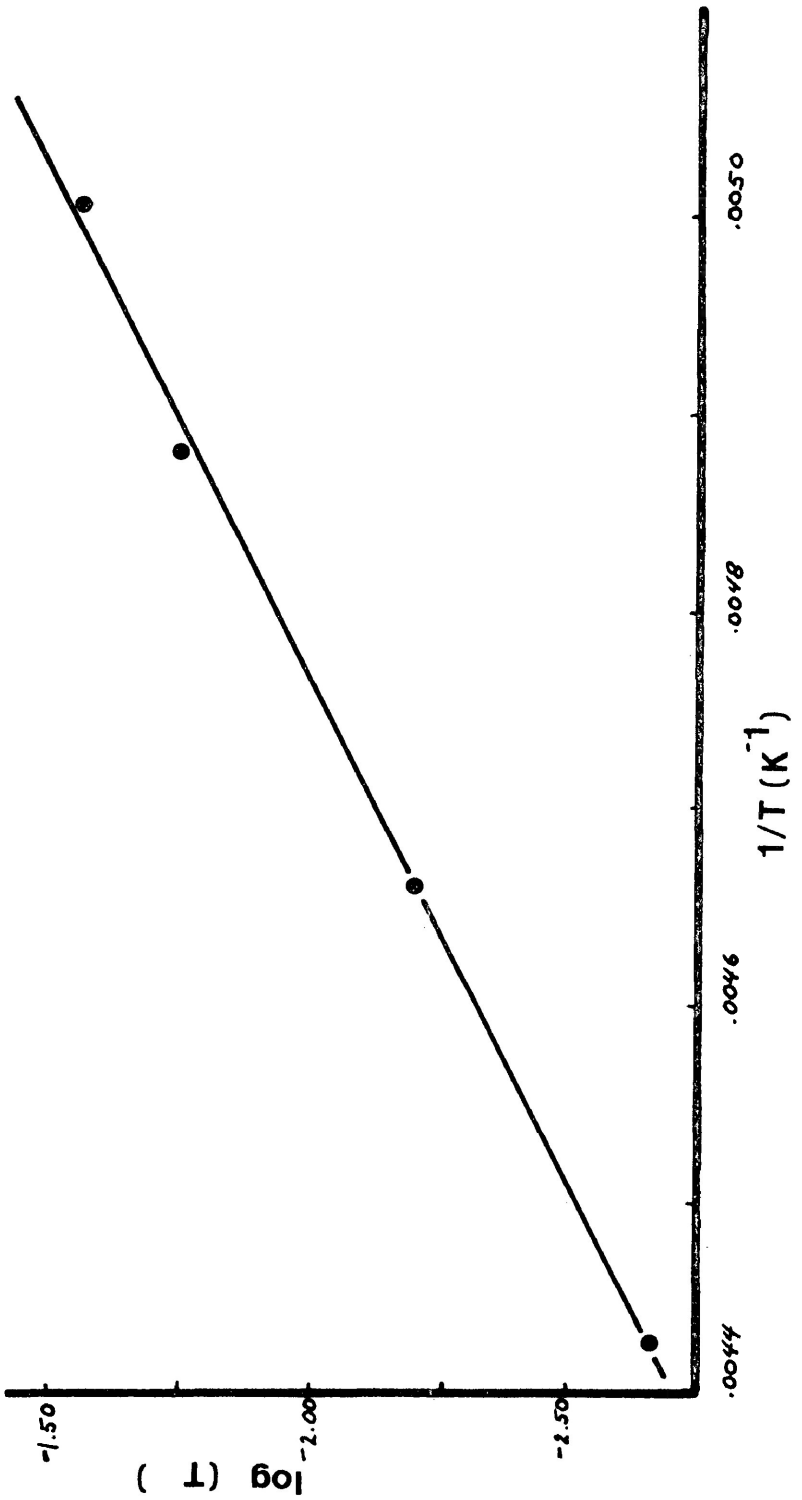

Figure IV-18 Eyring plot for the preceding graph.

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C H A P T E R V

INTRODUCTION

Over recent years, dielectric studies of carbonyl group containing compounds have been given considerable attention in the literature. These investigators have included both aliphatic and aromatic ketones as well as mixed aryl-alkyl systems. One such group of molecules to be rather extensively studied by various workers using a number of techniques has been the aromatic acetyls, the simplest of these being acetophenone (methyl phenyl ketone). The difficulty, however, has been in the serious disagreement between energy barriers recorded using different measurement techniques [1].

Fong and Smyth [2,3], for example, from dielectric studies in the microwave region, obtained enthalpies of activation of 4.2 to 6.2 kJ mol^{-1} for the acetyl group relaxations of α- and β-acetyl naphthalene, 4-acetyl o-terphenyl, 4-phenyl acetophenone, and 1,4,-diacetyl benzene all in benzene solutions. Madan [4,5] has observed similar low activation enthalpies of 4.2 to 12.1 kJ mol^{-1} for a number of aliphatic ketones in solutions of various non-polar solvents. The suggestion

by Madan is that the terminal carbonyl group rotation is the dominant intramolecular process. While this seems consistent with the observed behavior of some other aliphatic ketones studied by Crossley [6,7] and Smyth et al, [8], it has been reported from far-infrared studies of acetophenone in the gas phase that this molecule has a free energy barrier, ΔG_E, of 13.0 kJ mol^{-1} [9].

Grindley et al, [10], using n.m.r. data obtained for para-substituted acetophenones estimated a rotational barrier of 26.0 kJ mol^{-1} for the acetyl group in acetophenone itself. This can be compared to theoretical calculations by Hehre and coworkers [11] of 18.4 kJ mol^{-1}. Walker et al, [12], have reported barriers as high as 50 kJ mol^{-1} for the acetyl group relaxation in heterocyclic molecules such as N-acetylimidazole. This is in good agreement with McLellan's work with N-acetylindole, also in polystyrene, for which he reported a barrier of 48 kJ mol^{-1} [13].

In view of these disagreements found in the literature values for the energy barriers to carbonyl containing group rotations, a number of compounds

was studied in this relatively new media, glassy o-terphenyl, with the aim of demonstrating a conjugatively-based predictability to Eyring parameters for carbonyl rotations in certain compounds previously cited in the literature.

All studies were carried out in (1) dilute solutions of glassy o-terphenyl, or (2) as the pure compressed solid (see Chapter III). These systems were studied more widely to determine if some comment could be made on solvent effects to group relaxation processes of the type previously mentioned.

When possible, relevant data collected by other researchers will be presented to demonstrate clearly the importance of conjugative effects in determining observed energy barriers for carbonyl-containing flexible molecules.

As well, the possibility of multiple process overlap is considered in terms of weight factors for the molecular and intramolecular processes possible for flexible molecules studied in a given solvent (polystyrene). The results of a computer simulation of these factors will be presented in the discussion section of this chapter.

EXPERIMENTAL RESULTS

All molecules studied in this section were commercially prepared. The frequency range over which the studies were carried out was 10^2 to 10^5 Hz. The upper and lower temperature ranges were, in the former case, limited to the solvent system used and, in the latter case, near liquid nitrogen temperatures of $\sim$77 K.

Located at the end of this section, Figure V-1 illustrates structures of all compounds studied by this author for this chapter of the thesis.

Table V-1 is a collection of all referred to data obtained through the study of solutes in glassy o-terphenyl in the discussion section of this chapter. Table V-2 presents data obtained from compressed solid studies of molecules by this author using the technique described in Chapter III of this thesis as well as relevant data obtained from the literature.

TABLE V-1 Flexible molecules studied in glassy o-terphenyl.

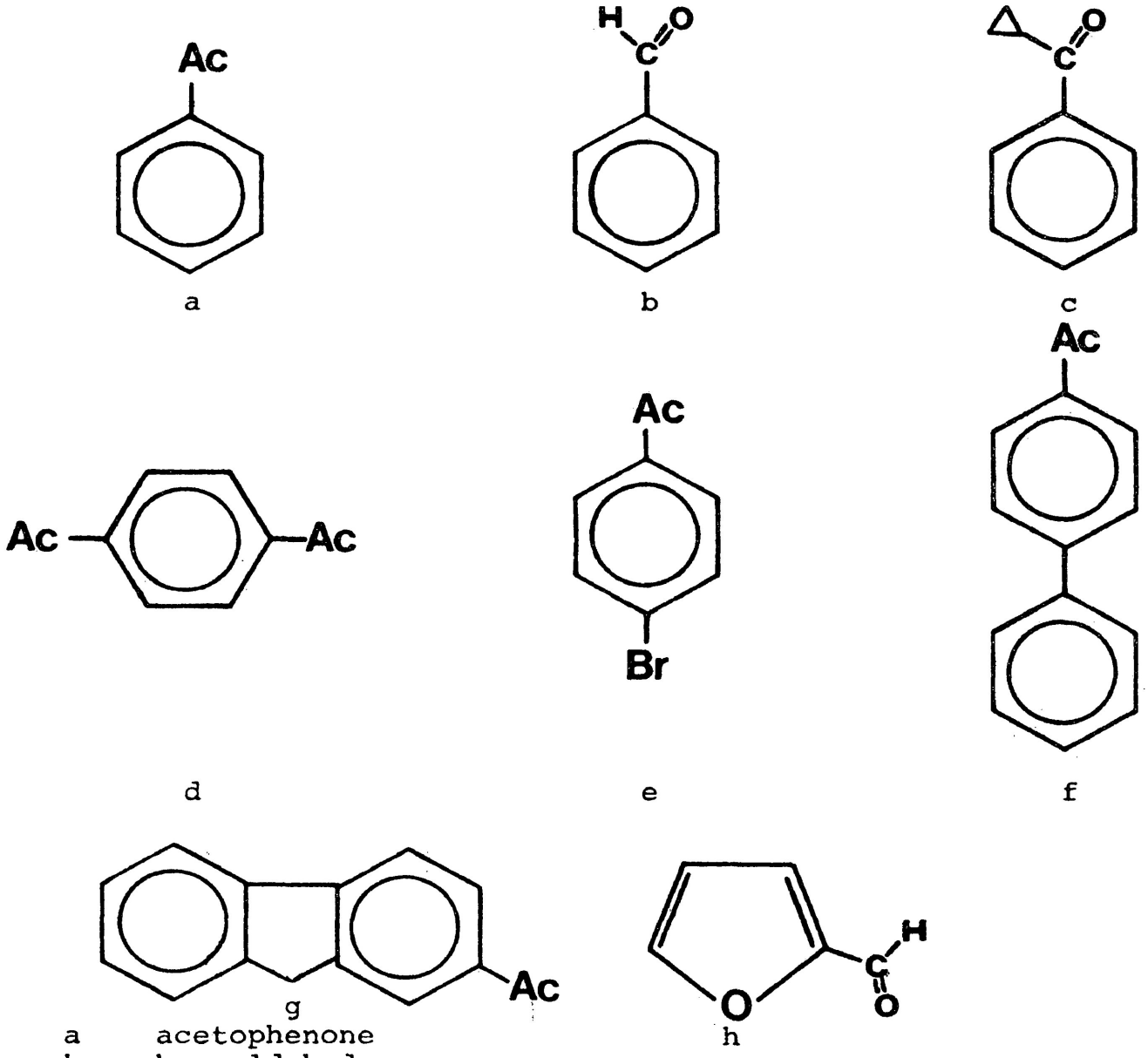
Molecule	T(K)	$\log f_{max}$	$\bar{\beta}$	$\tau_{200\,K}$ (s)	$\Delta G_{200\,K}$ (kJ mol^{-1})	ΔH_E (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})
acetophene	188.1-209.7	3.01-3.89	.25	4.58×10^{-8}	31.7	30 ±5	-7 ±25
benz-aldehyde	182.6-208.4	3.38-4.46	.36	1.10×10^{-5}	29.3	28 ±3	-3 ±14
cyclopropyl phenyl ketone	152 192	2.81-4.64	.20	1.97×10^{-6}	26.5	24 ±3	-14 ± 3
1,4-di-acetyl benzene	157.5-198.7	2.28-4.50	.23	3.69×10^{-6}	27.5	30 ±4	12 ± 5
4-bromo acetophenone	191 212	3.15-3.94	.21	4.80×10^{-5}	31.8	30 ±3	-11 ±15
4-acetyl biphenyl	178.6-204	3.00-4.22	.23	1.28×10^{-5}	29.6	33 ±5	16 ±24
2-acetyl fluorene	190.3-217.6	3.00-4.25	.20	5.20×10^{-5}	31.9	36 ±4	21 ±18
2-furalde-hyde	158.7-189.9	2.93-4.45	.22	2.21×10^{-6}	26.7	27 ±3	3 ± 9

TABLE V-2 Molecules studied in the compressed phase.

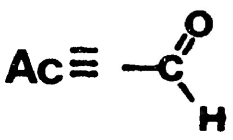
Molecule	T(K)	$\log f_{max}$	$\bar{\beta}$	$\tau_{200\,K}$ (s)	$\Delta G_{200\,K}$ (kJ mol^{-1})	ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
acetophenone	172 192	2.82- 3.63	0.5	2.10×10^{-5}	30.4	24 ±3	-34 ±16
benz- aldehyde	149 192	2.47- 4.47	0.6	2.9×10^{-6}	27.1	24 ±3	-15 ±5
1,4-diacetyl- benzene[a]	137 162	/	/	4.7×10^{-8}	/	27	16
4-acetyl- biphenyl[a]	154 192	/	/	6.1×10^{-7}	/	33	21
2-acetyl- fluorene[a]	212 242	/	/	1.2×10^{-4}	/	32	-24

N.B. compressed solid data designated with a superscript[a] refers to reference [1].

Figure V-1 Molecules in this chapter studied in glassy o-terphenyl.



a acetophenone
b benzaldehyde
c cyclopropyl phenyl ketone
d 1,4-diacetylbenzene
e 4-bromoacetophenone
f 4-acetylbiphenyl
g 2-acetylfluorene
h 2-furaldehyde



DISCUSSION

The relaxation times and activation parameters for the carbonyl compounds studied in glassy o-terphenyl are presented in Table V-1 in the experimental section of this chapter. The simplest of these ketones and the one which will be used as a basis for comparison is acetophenone.

The two systems in which these molecules have been studied are as ∿6% solutions of glassy o-terphenyl and as the pure compressed solid. When possible, studies of these or similar molecules in other media will be referred to as required. Since acetophenone and benzaldehyde are liquids (at room temperature), the compressed solid disks were prepared as described in Chapter III.

Acetophenone, as studied in glassy o-terphenyl, presented relaxation characteristics in good agreement with later studies by another worker in this laboratory using the same media [14]. This molecule has also been studied in polystyrene and, within experimental error, demonstrated enthalpies of activation of approximately

30 kJ mol^{-1}. Similar studies in the polyphenyl ether, Santovac , yield like results [14].

If we examine the structure of acetophenone in a profile view, one important point must be made. See Figure V-2.

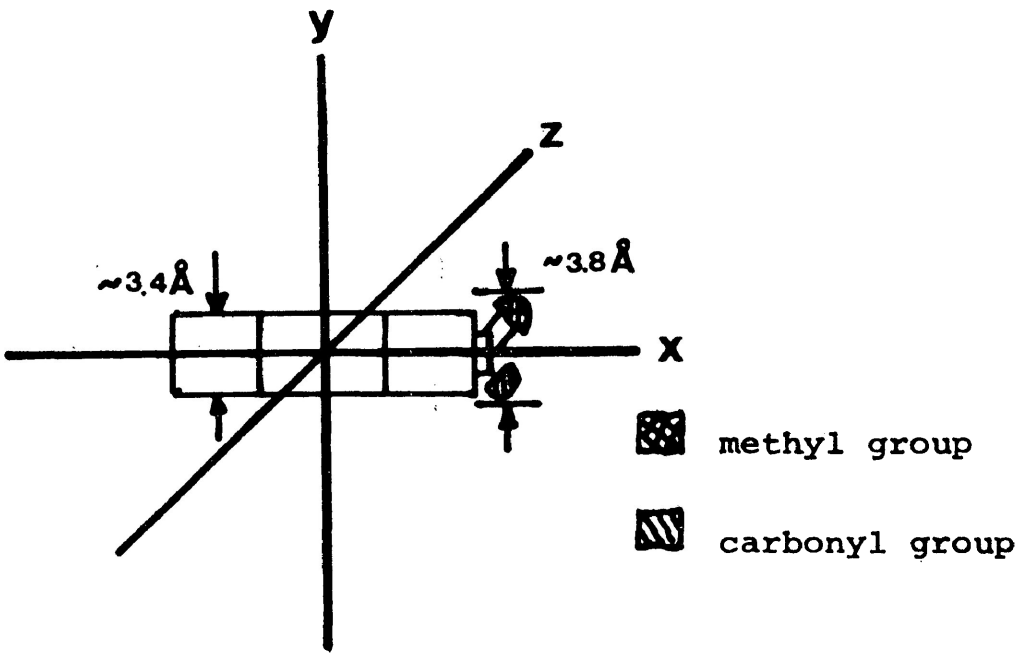


Figure V-2 Approximate molecular dimensions of the benzene ring relative to the acetyl group.

The thickness of the aromatic ring, approximately 3.4 $\mathring{A}^3$, is of the same order as the 'thickness' required by the rotation of the acetyl group during relaxation. With this in mind, it may be reasonable to ascribe the relative system insensitivity of group relaxation processes, at least in molecules of the substituted aryl-alkyl ketones type, where the alkyl substituent is small, to the free volume created within the solution by the molecular volume demands of the solute itself. This would certainly account for the similarities observed for aromatic acetyl and like group relaxations in the variety of media in which these molecules have been studied. It is with this in mind that a series of these molecules has been studied in o-terphenyl glass with the object of qualitatively relating enthalpies of activation to conjugative effects in the bond about which relaxation occurs.

Benzaldehyde has also been studied in a variety of media including glassy o-terphenyl, atactic polystyrene [15] and as the pure compressed solid. All compressed solid studies made by this author will be discussed toward the end of this chapter.

Within experimental error, the values are in good agreement with one another. The enthalpy of activation for benzaldehyde studied in glassy o-terphenyl also compares quite well with theoretical calculations provided by Hehre et al, [11] for benzaldehyde. They reported a value of 27.7 kJ mol^{-1} as compared to 28 ±3 kJ mol^{-1} from this work.

The slightly higher barrier observed in acetophenone over benzaldehyde in glassy o-terphenyl may be a result of the electron donating nature of the methyl group in the case of the ketone and even perhaps due to the size of the acetyl as compared to the aldehyde group: the former is larger, by virtue of the sp^3 hybridized carbon atom, and so must be considered more sterically demanding in terms of the ortho hydrogens on the benzene ring although this latter point probably plays little or no role in the observed increased barrier. The increased electron density in the aryl carbon-carbonyl carbon bond seems to have stiffened the bond increasing the barrier to acetyl group relaxation, and this is reflected in its Eyring parameters.

When the free energy barriers for acetophenone

and benzaldehyde are considered, there is a noticeable decrease between the value obtained for the ketone as compared to the aldehyde value ($\Delta G_{200\ K}$ = 31.7 kJ mol^{-1} in the former and 29.3 kJ mol^{-1} in the latter case).

The next molecule to be studied was cyclopropyl phenyl ketone. As a molecule studied in both atactic polystyrene and glassy o-terphenyl, the results were quite suprising. Sterically, the cyclopropyl ring is more demanding than a methyl group and even more so when compared to the aldehyde case. Depending upon the degree of steric interaction [16] with the aromatic ring, the cyclopropyl ketone moiety to a lesser or greater extent will be pushed out of the plane of the phenyl ring. In this case, the ability of the carbonyl group to conjugate with the π-clouds of the aromatic system of the benzene ring will be decreased. This would reduce the movement of π-electrons from the carbonyl group to the benzene ring and, thus would diminish the double bond character of the bond about which the group relaxes, lowering the enthalpies and free energies of activation, ΔG_E , for this molecule, if,

in fact, conjugative effects play the dominant role in this relaxation process.

The ΔH_E and ΔS_E values for the process observed in both glassy o-terphenyl and polystyrene are of the same order in both media: 24 ±3 kJ mol^{-1} and -14 ±3 J K^{-1} mol^{-1} in the former and 24 kJ mol^{-1} and -9 J K^{-1} mol^{-1} [17] in the latter case. The free energies of activation at 200 K are 26.5 kJ mol^{-1} and 25.4 kJ mol^{-1} in glassy o-terphenyl and polystyrene, respectively. Again, we observe a remarkable similarity between cyclopropyl ketone relaxation in these two quite different solvents. There is, however, another possibility.

It has long been recognized that in terms of both chemical and physical behaviors of the cyclopropyl ring, a close analogy to an olefinic double bond may be drawn owing to the increased electron density of this highly strained system [18]. This is borne out by the effect of cyclopropyl substitution on the stretching frequencies of the carbonyl group as observed in the infra-red absorption spectra of aromatic molecules of this type. Bellamy has reported the absorption of cyclopropyl phenyl ketone to be 1675 cm^{-1} [19,20,21] for the carbonyl group.

This may be compared to the absorption of acetophenone found at 1692 cm^{-1} [16]. Clearly torsional data from the far infrared region would likely reflect more accurately the degree of double bond nature, or, if you will, electron density of the bond about which relaxation occurs. Very little work, however, has been reported in these types of systems so shifts in carbonyl stretching frequencies have been used to reflect the relative degree of conjugation into which the carbonyl double bond has entered. This seems to reflect the electron density and hence the 'stiffness' of the bond through which relaxation occurs.

One would be remiss not to consider the possibility of molecular contribution in flexible molecules of this type. A molecule of similar size to cyclopropyl phenyl ketone, namely benzotrichloride, has also been studied in both o-terphenyl and atactic polystyrene. In the former case, the entropy and free energy values (the latter at 200 K) are at the high thermal limits of glassy o-terphenyl. They are 36 and 34 kJ mol^{-1}, respectively. In the latter case, a molecular process has been characterized for benzyltrichloride in polystyrene [17]. The temperature region over which the process has been

observed is 147 to 173 K, some 20 K lower than the region where cyclopropyl phenyl ketone absorption has been found in glassy o-terphenyl. As well, the ΔH_E and ΔS_E values of 20 kJ mol^{-1} and -26 J K^{-1} mol^{-1} are lower than those reported for the flexible molecule in glassy o-terphenyl. It would seem quite reasonable to ascribe the relaxation behavior in this flexible molecule to cyclopropyl ketone group relaxation with little molecular contribution. Observed dipole moments of 0.87 to 1.24 D over the temperature region, for which the process has been observed in polystyrene in comparison with those of the acetyl group rotation in acetophenone (1.24 - 1.36 D for temperatures of 162.0 - 181.1 K) [17], tend to suggest that similar processes are at work here. The value of $\sim$24 kJ mol^{-1} for the enthalpy of activation seems reasonable for the group relaxation of cyclopropyl phenyl ketone in both o-terphenyl and atactic polystyrene glasses.

Weight Factor Simulations

This would seem a logical point to break the discussion of experimentally observed results per se

and explore the nature and effects of overlapping processes in flexible molecules. The preceding is an example where the comparable-sized, rigid molecule, in at least one of the solvent systems (polystyrene), has Eyring parameters similar to those observed for its flexible counterpart.

Budó analysis [22], which has been discussed to a limited extent in Chapter II, relies on the assignment of weight factors of C_1 and C_2 for the molecular and group relaxation contributions, respectively in order to resolve 'overlapping' molecular and intramolecular processes. For the sake of convenience, a computer simulation has been developed which, written in the APLSF language, (see Appendix at the end of this thesis) calculates the molecular and intramolecular dielectric loss for a flexible molecule and plots each of these curves, plus the sum of the two, on one graph. In this way, the 'observed loss data' which would be resolved by Budó analysis more clearly shows the effect not only on the shape but on the interpreted loss maximum for the composite curve, the latter aspect being much more to the point as Eyring parameters depend

upon accurate loss maxima evaluations.

Certain assumptions were made to simplify the program. Firstly, the data were assumed to fit a modified Debye dispersion where the weight factors, C_1 and C_2, and the relaxation times, τ_1 and τ_2, are taken into account. Secondly, an arbitrary dispersion ($\varepsilon_o - \varepsilon_\infty$) of 0.1 was taken. Thirdly, the molecular weight factor, C_1, was varied from 0.10 to 0.45. Relaxation times for the group and molecular relaxation processes were taken from data obtained at a fixed temperature for (in the case of the relaxing group) acetophenone [23] and in the case of the relaxing molecule, the similarly sized iodobenzene [17], both studied in polystyrene.

Curves were then generated for a number of C_1 values. The suprising fact is that while the shape of the overall curve changed in terms of observed broadening, the actual $\log f_{max}$ value varied little. A representative set of curves, Figure V-3, is included to illustrate the point when C_1 was set at 0.35, where 0.35 is the C_1 as calculated for acetophenone from group moments [17].

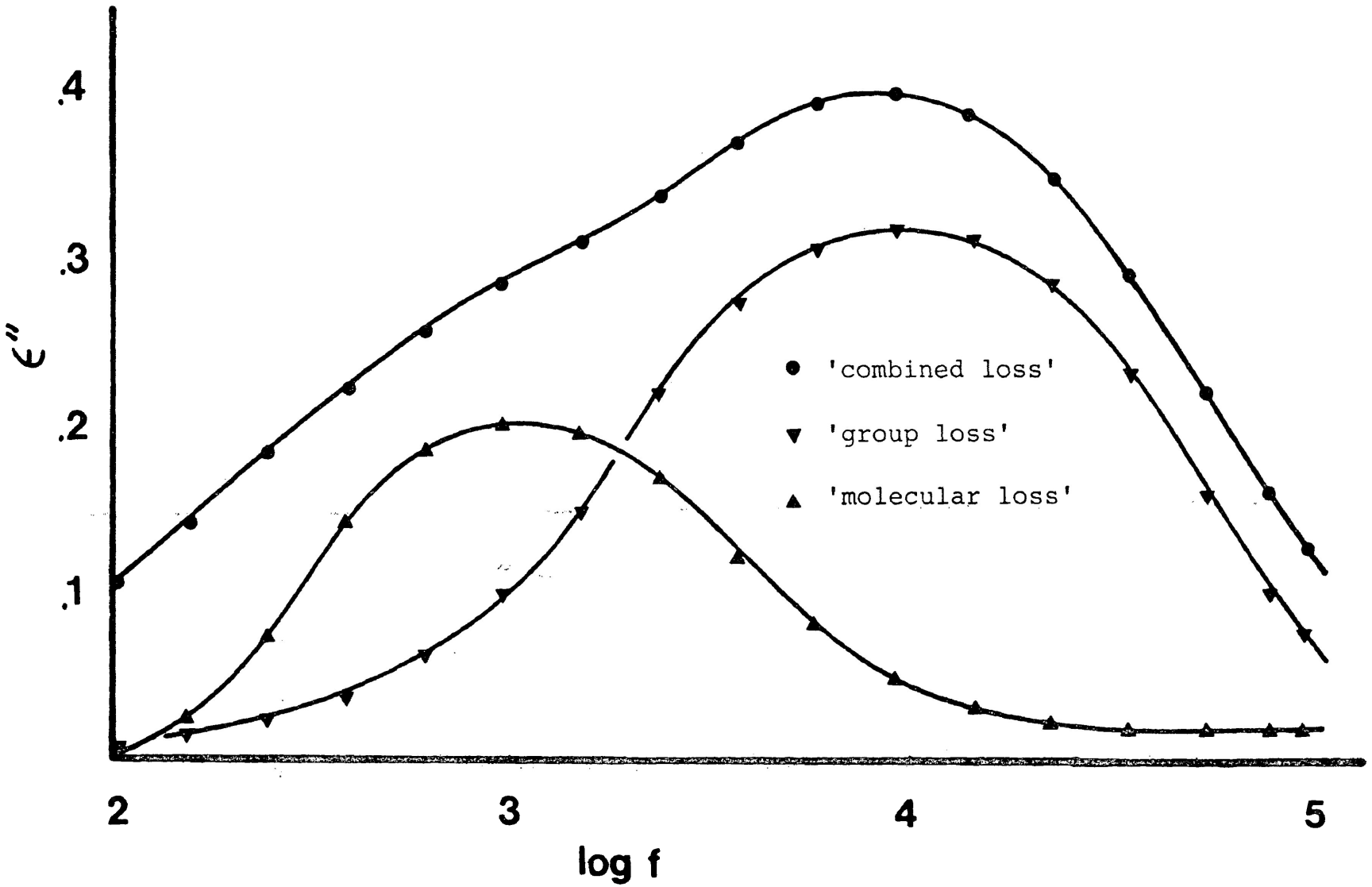


Figure V-3 Simulated loss curves as described in the text. Note, that the position of the loss maximun for the 'combined loss' curve has changed little from that of the 'group loss' curve, at C_1=0.35. (see Appendix, end of thesis for programme SIM[1] with which these values were calculated)

Another type of overlap which may play a particularly important role in evaluating the low loss dielectric process in flexible molecules is the magnitude of the 'tail ends' of the alternate loss process, even when the actual loss maxima may be well removed from the process under study.

Thus, the 'completely separated processes' which has been the goals of researchers working with flexible molecules for years may not ensure the certain accuracy of the Eyring parameters determined for each process if there is a large difference between the magnitudes of the losses observed with each process. Chapter VI more clearly illustrates these very points.

Para-halo substitution has also been a focus of study in much of the literature concerned with flexible relaxation. Farmer and Walker [24] studied a number of mono- and para-halo-substituted benzene compounds as cyclohexane solutions largely at 313 K over a wide frequency range. They determined that for p-bromoacetophenone, the τ_1 value of 26 ps reasonably represents a predominantly group relaxation process.

McLellan [25] studied this molecule in poly-styrene but felt the Eyring paramaters represented over-lap between the molecular and intramolecular process.

The ΔH_E, ΔS_E, and $\Delta G_{200\ K}$ obtained by this author's study of p-bromoacetophenone in glassy o-terphenyl are, within experimental error, identical to those observed for acetophenone studied in the same media. As well, the temperature regions and $\log f_{max}$ values for these two molecules, p-bromobenzophenone and acetophenone, are 188.1-209.7 K and $\log f_{max}$ 3.01 to 3.89 in the latter case and 191 to 212 K and $\log f_{max}$ 3.15 - 3.94 in the former case.

These values seemingly represent primarily group relaxation on the part of the acetyl group. It would also seem that the para-bromo substituent has not appreciably altered the electron density of the bond about which relaxation occurs and hence the barrier to that relaxation process.

1,4-di-Acetylbenzene is a rather interesting molecule and has been well studied in a number of media. It is novel in that two possible orientations exist for the two planar para-acetyl groups. Figure V-4 illustrates both the cisoid and transoid configurations of this molecule.

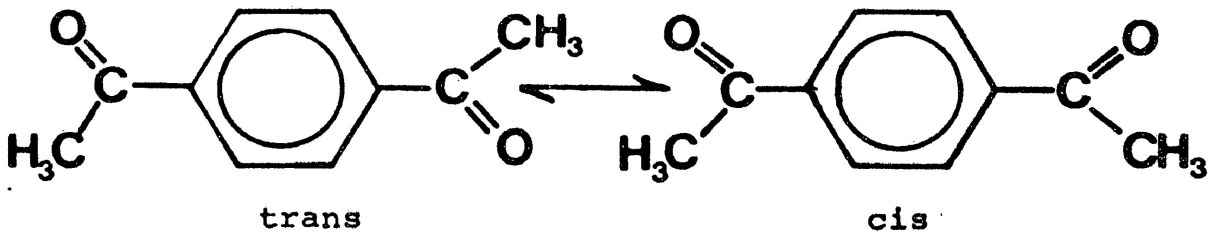


Figure V-4

It is likely that this molecule is undergoing predominatly group relaxation if we compare its Eyring parameters against those of a rigid molecule of a slightly smaller size, namely 4-bromotoluene, both studied in polystyrene. The relaxation times for this rigid molecule at 150, 225, and 300 K are approximately two orders of magnitude longer than those of 1,4-diacetylbenzene which is not what one would expect if the molecule were undergoing predominantly molecular relaxation. Still, the two possible relaxation candidates in this case are, in

the group sense, the cis or trans isomers.

A predominantly transoid configuration would have associated with it several specific physical characteristics. Firstly, the dipole moments expected with opposing carbonyl functions would tend to cancel one another out and so the experimentally observed dipole moment for this molecule should be small. Similarly, media sensitivity should be minimal as the dipole involved in the molecular relaxation about the long axis would also be small. Walker et al [27] noted a comparison of the τ_o values of 1,4-diacetylbenzene in benzene as compared to the same molecule studied in liquid o-terphenyl which revealed an appreciable increase in the relaxation times, (16.2 ps and 154 ps at 333 K, respectively). Such lengthening of the observed relaxation time for an increase in macroscopic viscosity from $\sim$0.6 to 25 cP indicates a substantial contribution from the molecular reorientation process. This is in agreement with work by Fong and Smyth [28] who suggest a very high (0.9) molecular weight factor. The actual observed dipole moment values for this molecule in liquid o-terphenyl are of the order of 2.8 D.[25] This might tend to suggest a cisoid predisposition in the cis-trans equilibrium which likely exists between the two isomers. Thus, the certainty of the enthalpy of activation

for this molecule both in glassy o-terphenyl (30 ±4 kJ mol^{-1}) and atactic polystyrene (29 kJ mol^{-1}) being purely representative of the group relaxation process is open to some speculation.

When the para-substituent is a phenyl group, the observed relaxation process, over the temperature region 178.6 to 204.0 K and with an enthalpy of activation of 33 ±5 kJ mol^{-1} in glassy o-terphenyl, seems not to have changed a great deal over that observed for acetophenone itself. 4-Acetylbiphenyl has also been studied in atactic polystyrene and as the compressed solid [1].

In polystyrene, this molecule has shown both a high and a low temperature absorption process. The enthalpy of activation for the lower temperature process is 30 kJ mol^{-1} while the same parameter for the higher temperature process is 68 kJ mol^{-1} . The temperature region, over which the lower energy process occurs, is 146 to 172 K and would seem to be approximately 30 K lower than the process observed in glassy o-terphenyl. As well, the relaxation time in seconds for this process is several orders of magnitude greater at ∿200 K in o-terphenyl than in polystyrene (1.3×10^{-5} s in the former case and 2.9×10^{-8} s in the latter). More significant

perhaps is the fact that the higher temperature process has a relaxation time at 200 K of 2.6×10^{1} s.

On comparison with a similar-sized rigid molecule, 4-nitrobiphenyl, also studied in polystyrene, the relaxation time for this clearly molecular relaxation process occurring over the temperature region 294 to 312 K is 4.5×10^{1} s at $\sim$200 K while the ΔH_E value is 86 kJ mol^{-1} [1]. Clearly the lower temperature absorption in the polystyrene system of dispersed 4-acetylbiphenyl is a group process while the higher temperature process, the ΔH_E of which is 68 kJ mol^{-1}, must be molecular in nature. From the study of o-terphenyl glass presented in Chapter IV, we can clearly assume that the molecular process of 4-acetylbiphenyl is well outside the working temperature range of glassy o-terphenyl (i.e. well above the Tg of o-terphenyl glass).

Another molecule studied in both glassy o-terphenyl and atactic polystyrene is 2-acetylfluorene. This molecule, as studied by McLellan and Walker [1], provides two regions of absorption in polystyrene.

The lower temperature process, over 158 to

177 K, has an enthalpy of activation of 32 kJ mol^{-1} and an entropy factor of 28 J K^{-1} mol^{-1}. This compares well with this author's study of the same molecule in glassy o-terphenyl, the results of which are presented in Table V-1 in the experimental section of this chapter (ΔH_E ∿36 ±4, ΔS_E ∿21 ±18).

While the relaxation time at ∿200 K differs between the two media, 1.3×10^{-5} s in glassy o-terphenyl and 2.2×10^{-7} s in atactic polystyrene, this often seems to be the case within the two media. The higher temperature process, again well outside the useful range of glassy o-terphenyl, covers 317 - 337 K and has an enthalpy of activation of 89 kJ mol^{-1} with an entropy factor of 100 J K^{-1} mol^{-1}.

On close examination of the ΔH_E values for the molecules presented in Table V-1, one point should be noted. Within experimental error, and excluding cyclopropyl phenyl ketone, these molecules all show similar enthalpy of activation values. At the risk of over-interpretation of data, the order of increasing enthalpies of activation seems to be cyclopropyl phenyl ketone, benzaldehyde, acetophenone, 1,4-diacetylbenzene, p-bromo-

acetophenone, based on the facts that the absorption occurs at a higher temperature region, the $\Delta G_{200\ K}$ value is somewhat greater than in 1,4-diacetylbenzene, 31.8 versus 27.5 kJ mol^{-1} and the relaxation time is an order of magnitude greater, and finally, 4-acetylbiphenyl. 2-Acetylfluorene, as studied in glassy o-terphenyl, presented the largest ΔH_E value of any molecule studied in this system. Some question as to the accuracy of this value must be entertained as the sample was particularly difficult to study.

The 4-acetylfluorene/o-terphenyl solution seemed to crystallize even on rapid cooling and so presented a rather difficult sample to stabilize during the taking of measurements. Even with this in mind, several valuable points can be made.

First, in all the solutes discussed thus far, every indication is that the calculated Eyring parameters reflect intramolecular relaxation processes which are, within experimental error, in concert with data obtained by other workers studying these solutes in atactic polystyrene.

Second, there are certain limitations on the range of enthalpies and so on the types of relaxing groups which can be studied in glassy o-terphenyl. The glass transition temperature is certainly a limiting factor in the choice of glassy o-terphenyl as a solvent.

In order to further the conjugatively based enthalpy concept, work performed in this laboratory with heterocyclic molecules, which tends to suggest, at least in atactic polystyrene solutions, that the barrier to rotation of relaxing groups is largely dependent upon the double bond character of the bond through which rotation occurred, was examined in the hopes of finding a molecule having a group enthalpy of activation of the order of $\sim$36 kJ mol^{-1} in glassy o-terphenyl.

Khwaja _et al_ [12] have studied a number of heterocyclic flexible molecules in atactic polystyrene and, in certain cases, have demonstrated both the molecular and intramolecular relaxation processes within the same sample. In fact, the dielectric properties of four of the molecules studied gave both high and low temperature absorption processes and will be discussed in this chapter. Three of these molecules are heterocyclic aldehydes and

the fourth is an heterocyclic acetyl substituted molecule where the point of substitution is directly on the hetero-atom. Of these four molecules, the one which seemed to be the most likely to demonstrate a group relaxation process in glassy o-terphenyl was thiophene-carbaldehyde. This molecule showed two regions of dielectric absorption. The lower temperature process, 127 - 162 K, has the following Eyring characteristics: the enthalpy of activation for this molecule over this temperature range is 20 kJ mol^{-1} while the free energy of activation and relaxation times, both at 200 K, are 23 kJ mol^{-1} and 2.3×10^{-7} s respectively. These authors, by comparing similar sized, rigid, molecular behavior have been able to ascribe reasonably the higher temperature process to group relaxation and the lower temperature process to molecular relaxation.

The molecule which has the lowest barrier to group relaxation thiophene-2-carbaldehyde (ΔH_E = 44 kJ mol^{-1}) was chosen as the type of molecule which might test the limit of enhanced group relaxation in glassy o-terphenyl. This paper suggests that the unusually large ΔH_E values are a result of increased conjugation between the group and the α hetero-atom, in this case sulphur, and its high electron density, which contributes

to the electron density in the aldehyde group attached at the two position. With this in mind, it seemed reasonable that a less electron-rich hetero-atom might reduce the electron density in the carbon-carbon aldehyde bond and thus decrease the enthalpy of activation to aldehyde relaxation. The molecule chosen was 2-furaldehyde, as a 5% by weight solution in glassy o-terphenyl. The results have been presented in Table V-1.

Previous studies of 2-furaldehyde by n.m.r. [29] and ultrasonic absorption [30] techniques have yielded an activation enthalpy of 42.7 to 46.0 kJ mol^{-1} to the internal rotation about the carbon-carbon bond that is adjacent to the carbonyl bond. Dielectric studies of this molecule yielded an enthalpy of activation of 45.6 ±3 kJ mol^{-1} and an entropy of 11 ±4 J K^{-1} mol^{-1} for a process observed over the temperature range 230 - 324 K. The free energy for this process at 200 K was 43 kJ mol^{-1}. Also, a low temperature absorption process in the range of 109 - 148 K has been observed in the frequency range of 10^2 to 10^5 Hz [32]. This yielded an activation enthalpy and entropy of 14 kJ mol^{-1} and -40 J K^{-1} mol^{-1} respectively. On comparison with the corresponding parameters of 16.4 kJ mol^{-1} and 1.4 J K^{-1} mol^{-1} for a rigid molecule of fairly

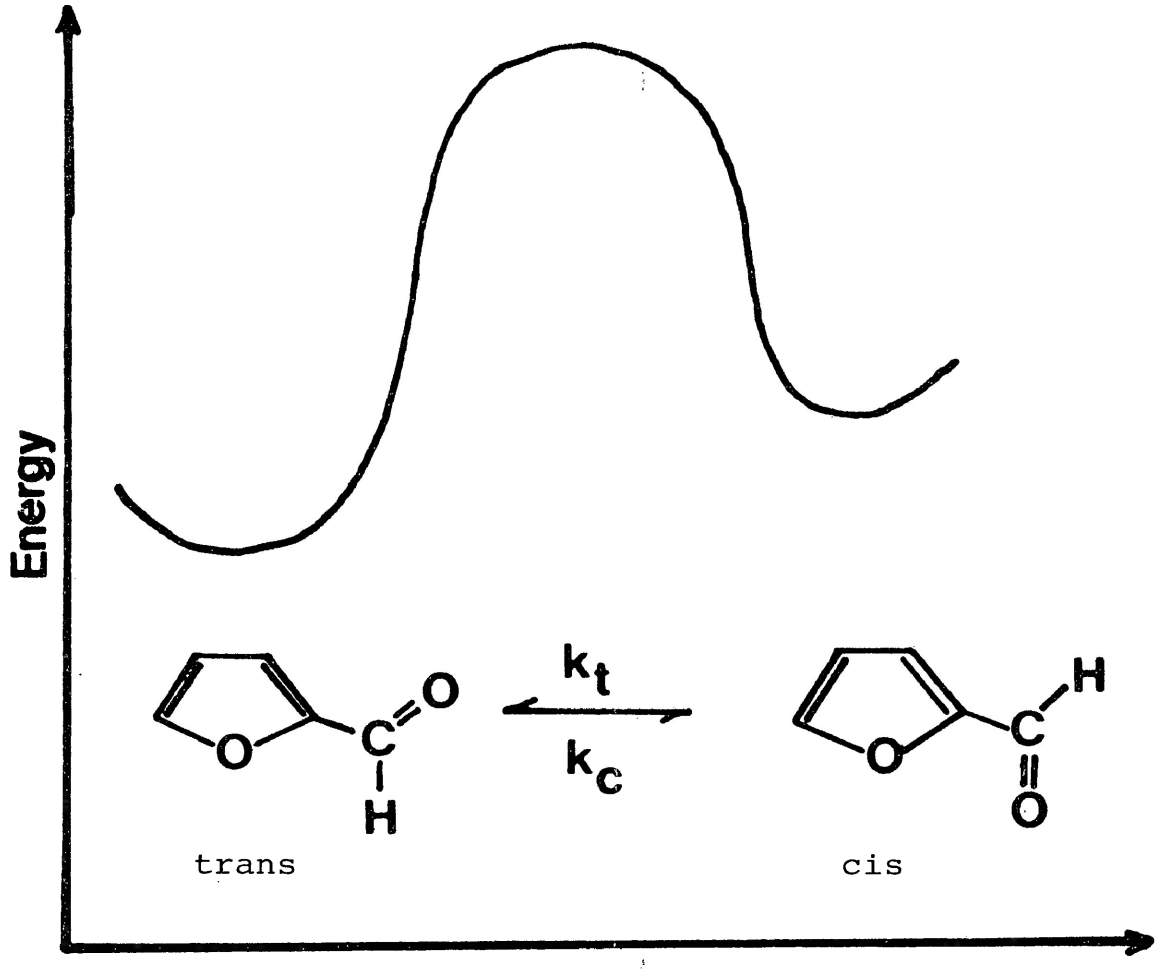


Figure V-5 Energy of activation diagram for the relative energy distribution between the cis and trans isomers of 2-furaldehyde. Note the asymmetry of the curve with respect to the two equilibrium positions A and A'.

similar size and shape, namely o-dichlorobenzene also studied in atactic polystyrene [31], this leaves little doubt that the lower temperature process is, in fact, due to molecular relaxation of 2-furaldehyde in atactic polystyrene.

It should be pointed out that the energy of activation diagram for this molecule is asymmetrical, see Figure V-5, and so kinetic calculations and population distributions of the possible cis and trans isomers can be used to modify the free energy calculations of data obtained by the various means previously mentioned. The Eyring rate expression and hence the enthalpy and entropy values calculated have been shown, at least in the case of this molecule, to be relatively unaffected by this asymmetry. That is to say, the factors to be introduced by the more rigorous treatment affect the results by a factor less than the expected experimental error and so will not be considered further.

From the data presented in Table V-1 for 2-furaldehyde, the enthalpy and entropies of activation for this molecule are 27 ±3 kJ mol^{-1} and 3 ±9 J K^{-1} mol^{-1}

respectively. Although the enthalpy value here of 27 ±3 kJ mol^{-1} is considerably higher than the value obtained by S. P. Tay *et al* (27 ±3 kJ mol^{-1} versus 14 kJ mol^{-1}), the free energy of activation at 200 K and the enthalpy value are too low to be considered the intramolecular process. (In polystyrene, T_{range} = 230 - 324 K $logf_{max}$ range = 2.1 to 5.3, ΔH_E = 45.6 ±1.1 kJ mol^{-1}, ΔS_E = 11 ±4 $JK^{-1}mol^{-1}$ and ΔG_{200K}= 43.3 $kJmol^{-1}$ compared to results in glassy o-terphenyl, T_{range} = 158.7 - 189.9, $logf_{max}$ range = 2.93 to 4.45, ΔH_E = 27 ±3 $kJmol^{-1}$, ΔS_E=3 9 $JK^{-1}mol^{-1}$, and ΔG_{200k}=26.7 $kJmol^{-1}$).

From these data, it would seem clear that the intramolecular barrier for 2-furaldehyde is outside the useful range of glassy o-terphenyl. However, the molecular barrier, as reported by Walker *et al* [12], is observed at a temperature some 50 K lower than the results observed in glassy o-terphenyl. As a point of interest, the free energy at 150 K and the enthalpy of activation values were used in the empirical equations developed in the previous chapter.

Inasmuch as the molecular process for 2-

furaldehyde has been determined in glassy o-terphenyl, it seemed reasonable to apply the available equations developed in Chapter IV to see if this molecule behaves, in this medium, as the rigid molecules studied for this thesis.

On application of equation IV-1, which relates $\Delta H_{P.S.}$ to ΔH_{GOTP}, the following results are obtained:

$$\Delta H_{P.S.} = 0.50\ \Delta H_{GOTP} + 3.3$$

$$\Delta H_{GOTP} = \sim 27\ \text{kJ mol}^{-1}$$

$\Delta H_{P.S.}$ for the molecular process $\sim 14\ \text{kJ mol}^{-1}$

$\Delta H_{P.S.}$ calculated $= 16.8\ \text{kJ mol}^{-1}$

This is clearly, within experimental error, in excellent agreement with the rigid molecules studied. The value of this relationship seems, at least for the molecules studied, to be valid. Data for the low temperature process in polystyrene were not available to test all of the other relationships.

COMPRESSED SOLID STUDIES

Essentially two types of compressed solid studies have been reported in Table V-2. Of the five molecules studied as the pure solid, only two were liquids at room temperature and so required the special technique described in Chapter III.

Compressed solid studies were undertaken to try to determine accurate enthalpies of activation for (1) flexible molecules where molecular overlap was thought to be occurring and (2) to support, with measurements in other media, the ΔH_E values obtained for intramolecular motions. An important point to consider is the method of preparation. This seems to alter the magnitude of the Eyring parameters calculated from Fuoss-Kirkwood analysis of even symmetric loss curves.

As regards this last point, the ΔH_E values obtained from studies of disks prepared from solids at room temperature are in very good agreement with those values obtained in polystyrene.

Of the other molecules, acetophenone and benzaldehyde both show quite sharp ($\overline{\beta}$ $\sim$0.5 and $\sim$0.6, respectively) absorption curves from which seemingly accurate, but low ΔH_E values were calculated - seemingly accurate in that the log($T\tau$) versus ($1/T$ (K^{-1})) correlation coefficients were greater than 0.9600 and the error on these values at the 90% percent confidence interval was of the order of the experimental error i.e. $\sim\pm 3$ kJ mol^{-1}.

Clearly, the nature of the solid disk produced by this new method must be further explored to determine its validity as a research technqiue and also to see what variation exists in results obtained in terms of reproducability. It was hoped that a third liquid sample, namely cyclopropyl phenyl ketone, could be formed into a stable compressed disk, but this was not practicable. In addition, attempts to study 1-acetyl naphthalene as the compressed solid failed as this liquid tended to form a super-cooled liquid on cooling, and only at very low temperatures, i.e. $\sim$77 K did it finally crystallize. Needless to say, it was very difficult to prepare a powdered sample to compress, let alone study it as a

compressed solid at these temperatures. At the application of any significant pressure, the powder liquefied. and on release of that pressure solidified again, but the sample, in three attempts, was always a myriad of fractures, the dieletric characteristics of which were quite unstable. Future work with liquids below their freezing point may remedy many of these problems. At present, however, this seems to be a novel approach to a heretofore insurmountable limitation to compressed solid studies, namely that the sample be solid at room temperature.

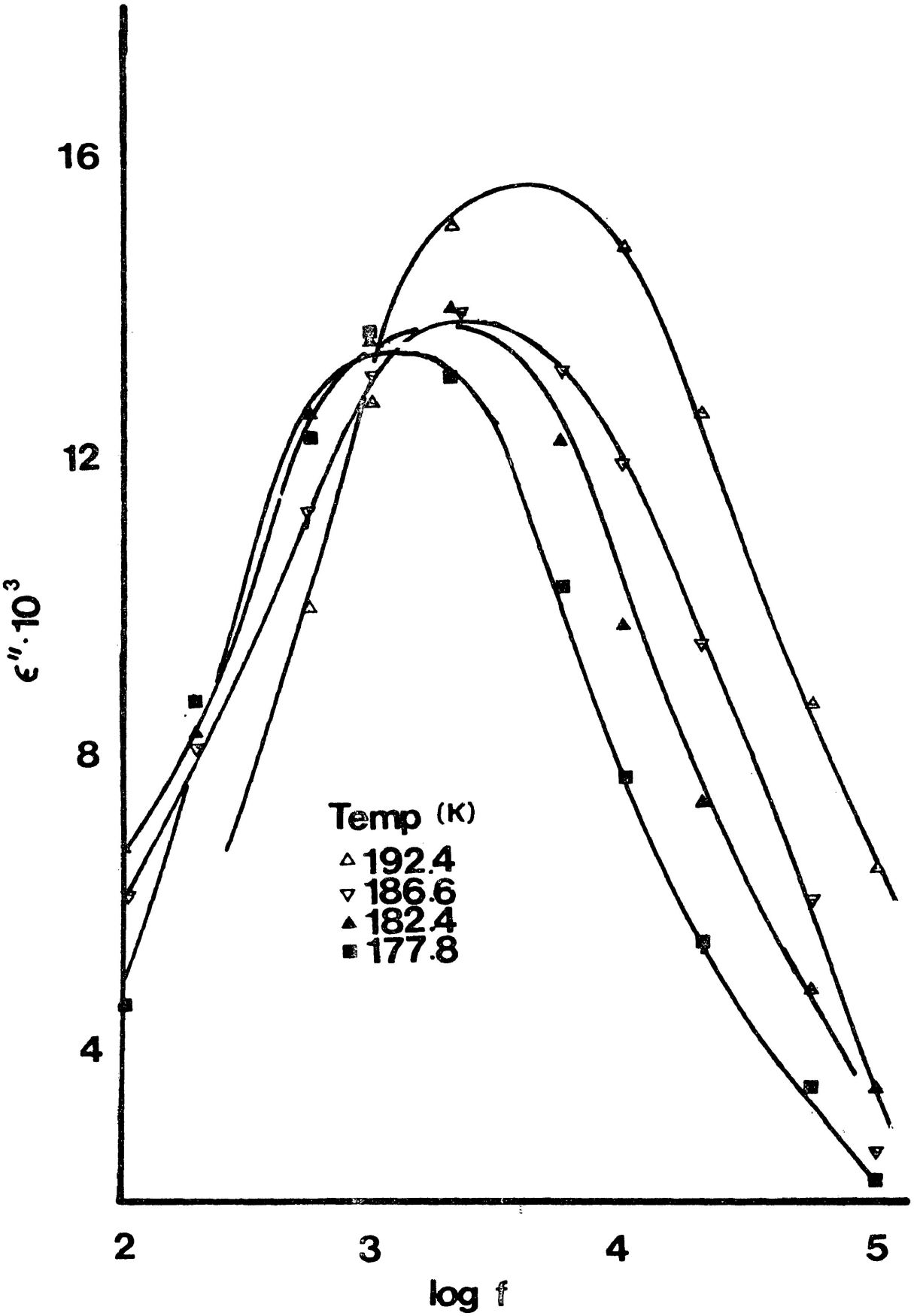


Figure V-6 Acetophenone as the compressed solid

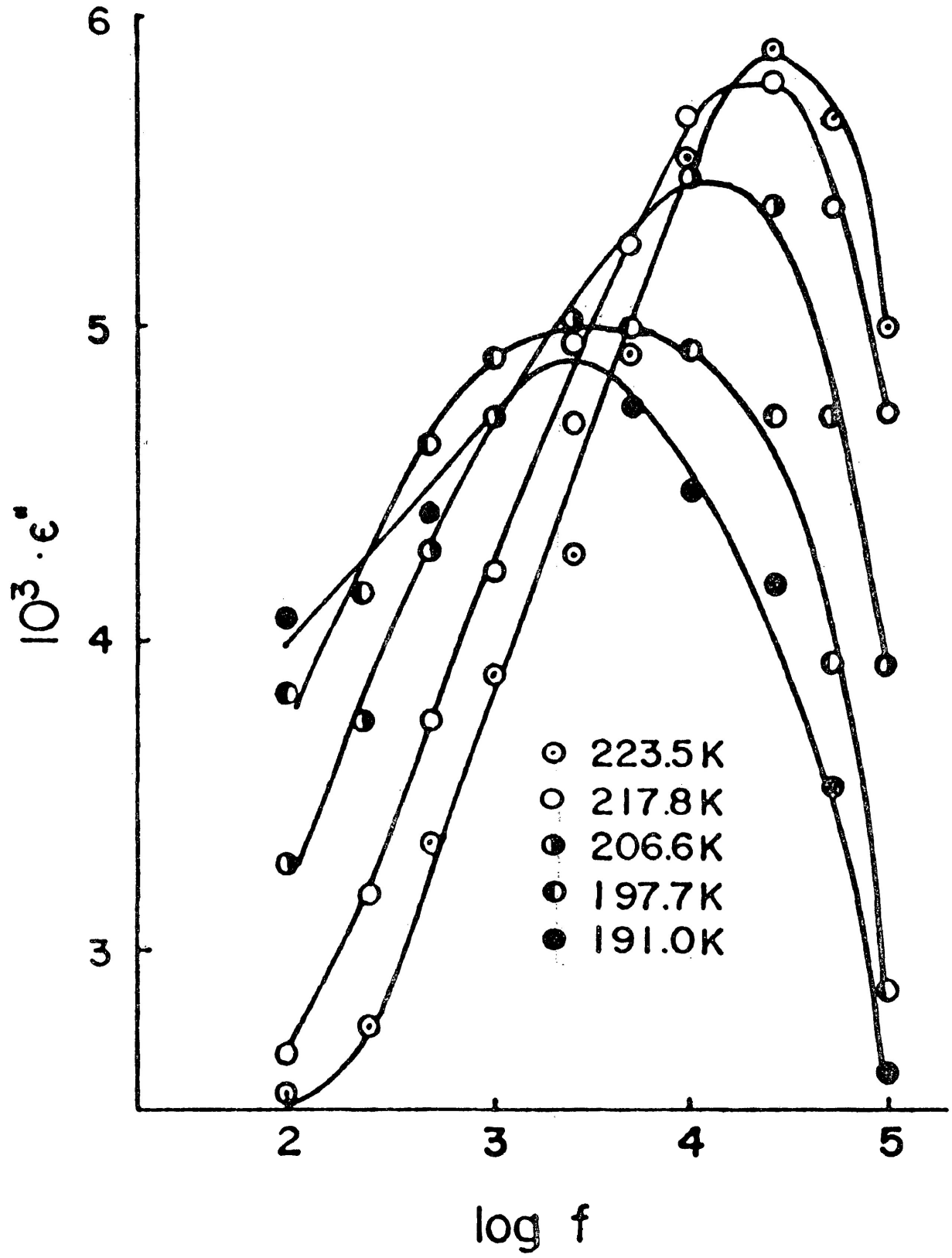


Figure V-7 Acetophenone loss curves for a 5% solution by weight in glassy o-terphenyl.

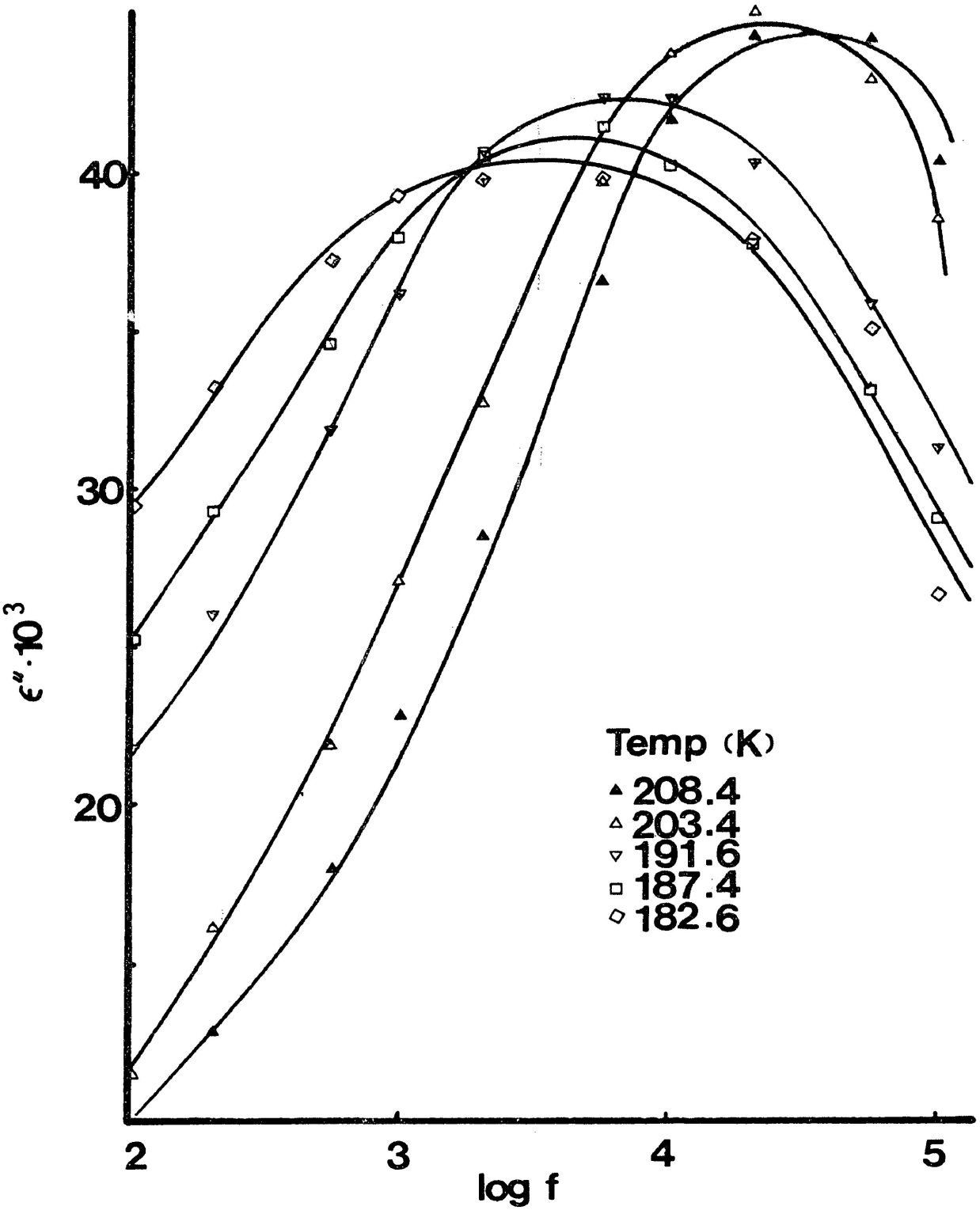


Figure V-8 Benzaldehyde loss curves as studied in a 5% by weight solution of glassy o-terphenyl.

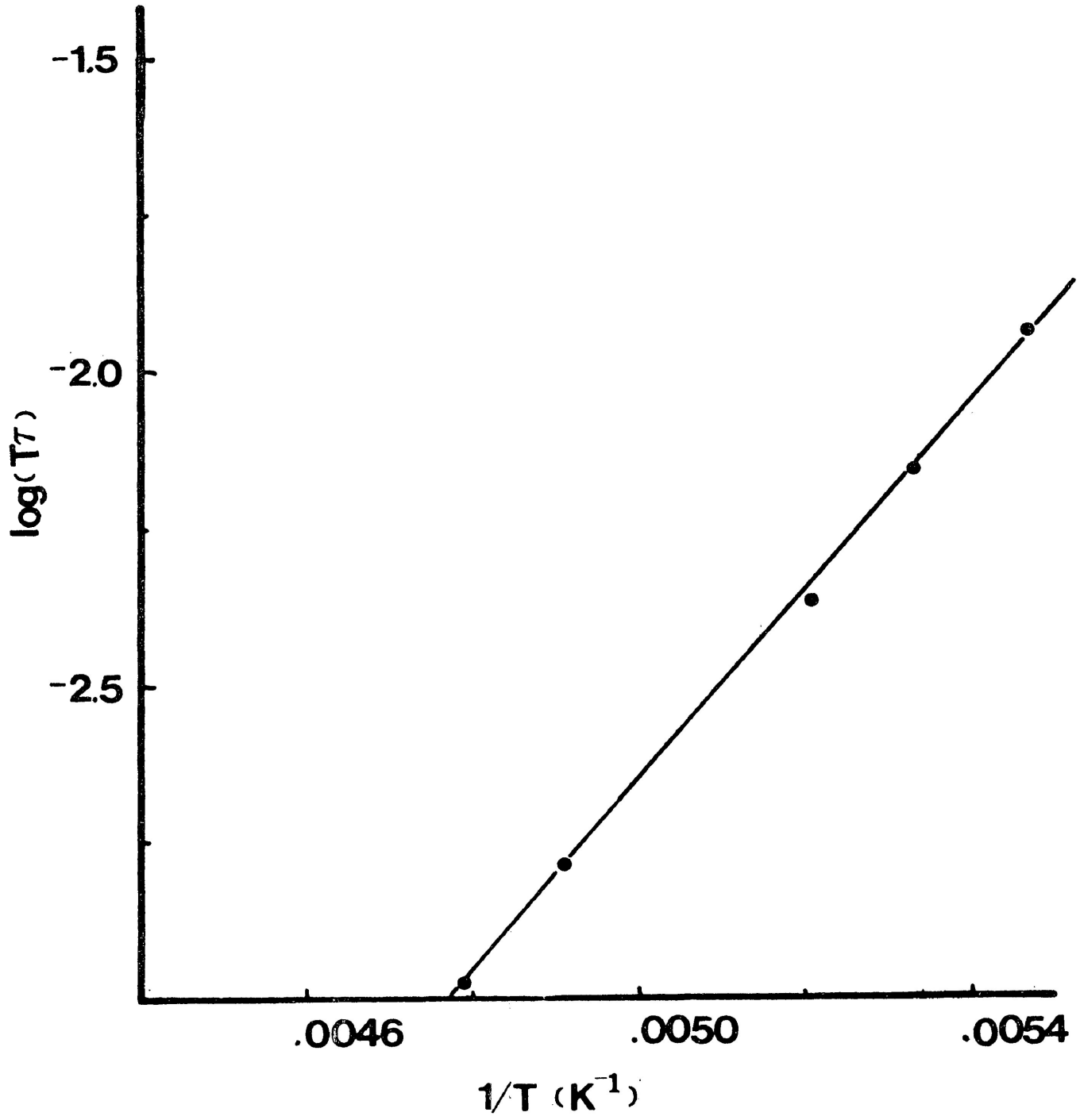


Figure V-9 Eyring plot of the absorption process observed in benzaldehyde (5% by weight in GOTP)

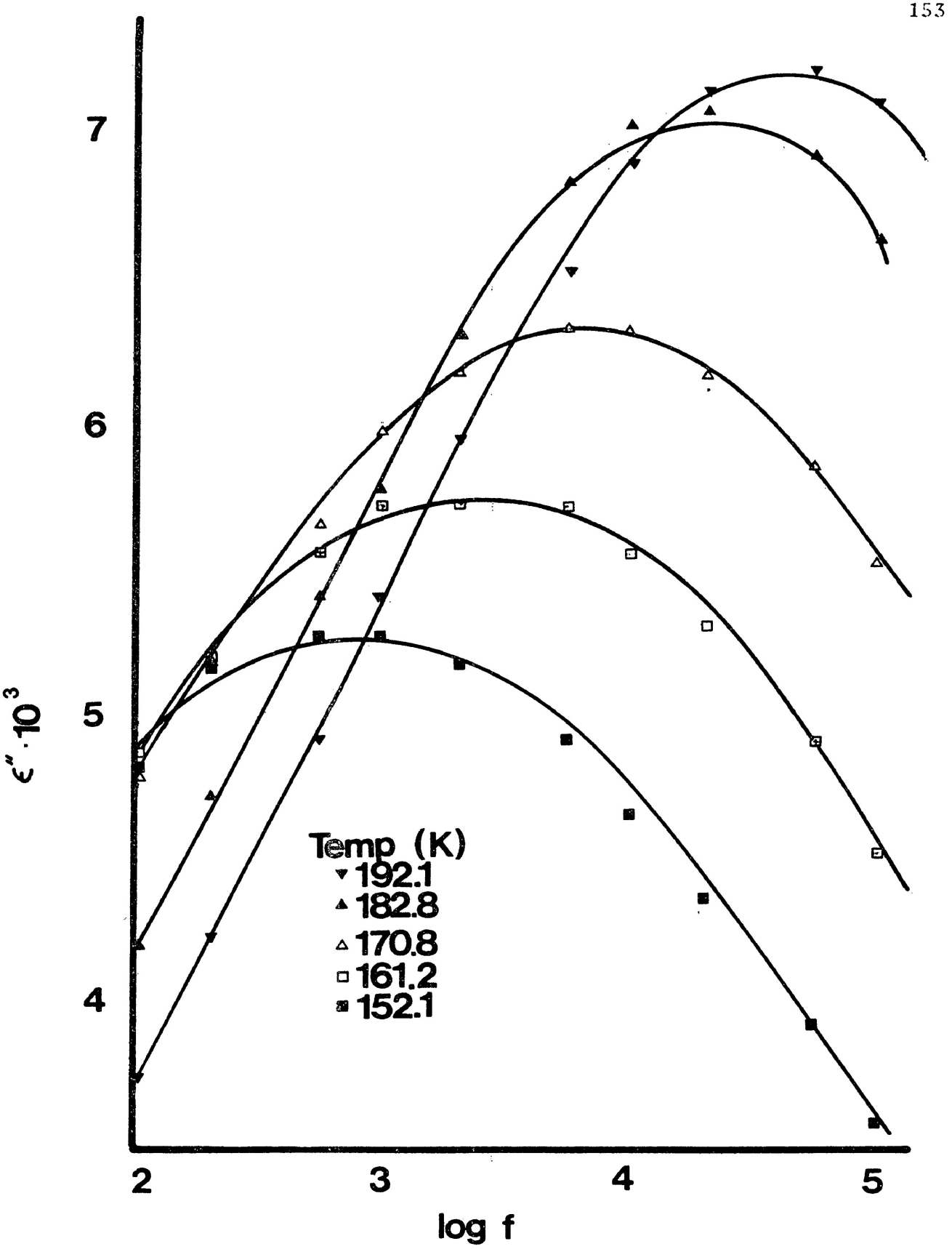


Figure V-10 Loss curves for cyclopropyl phenyl ketone (5% percent in GOTP)

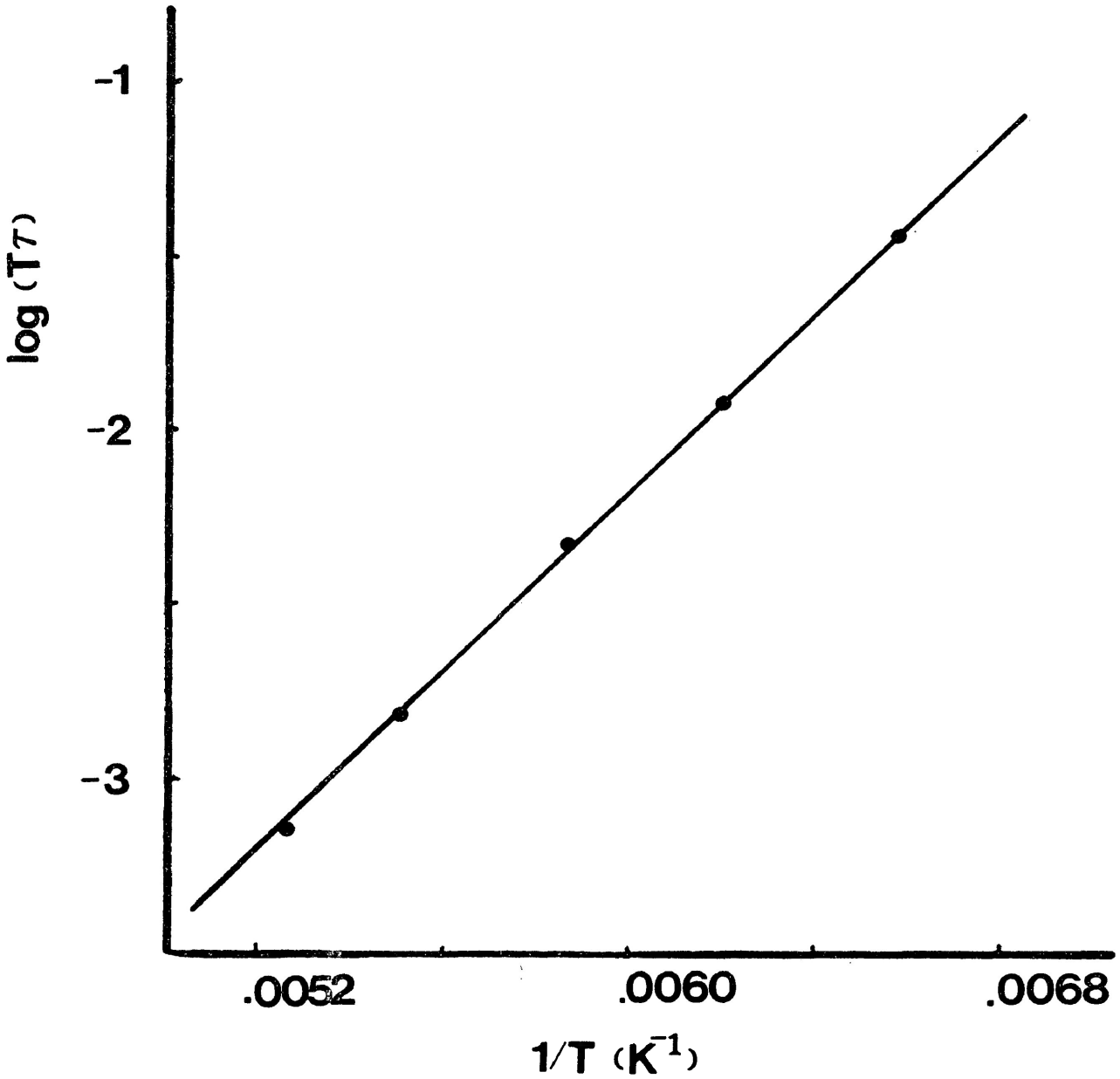


Figure V-11 Eyring plot for the process observed with cyclopropyl phenyl ketone (5% by weight in GOTP)

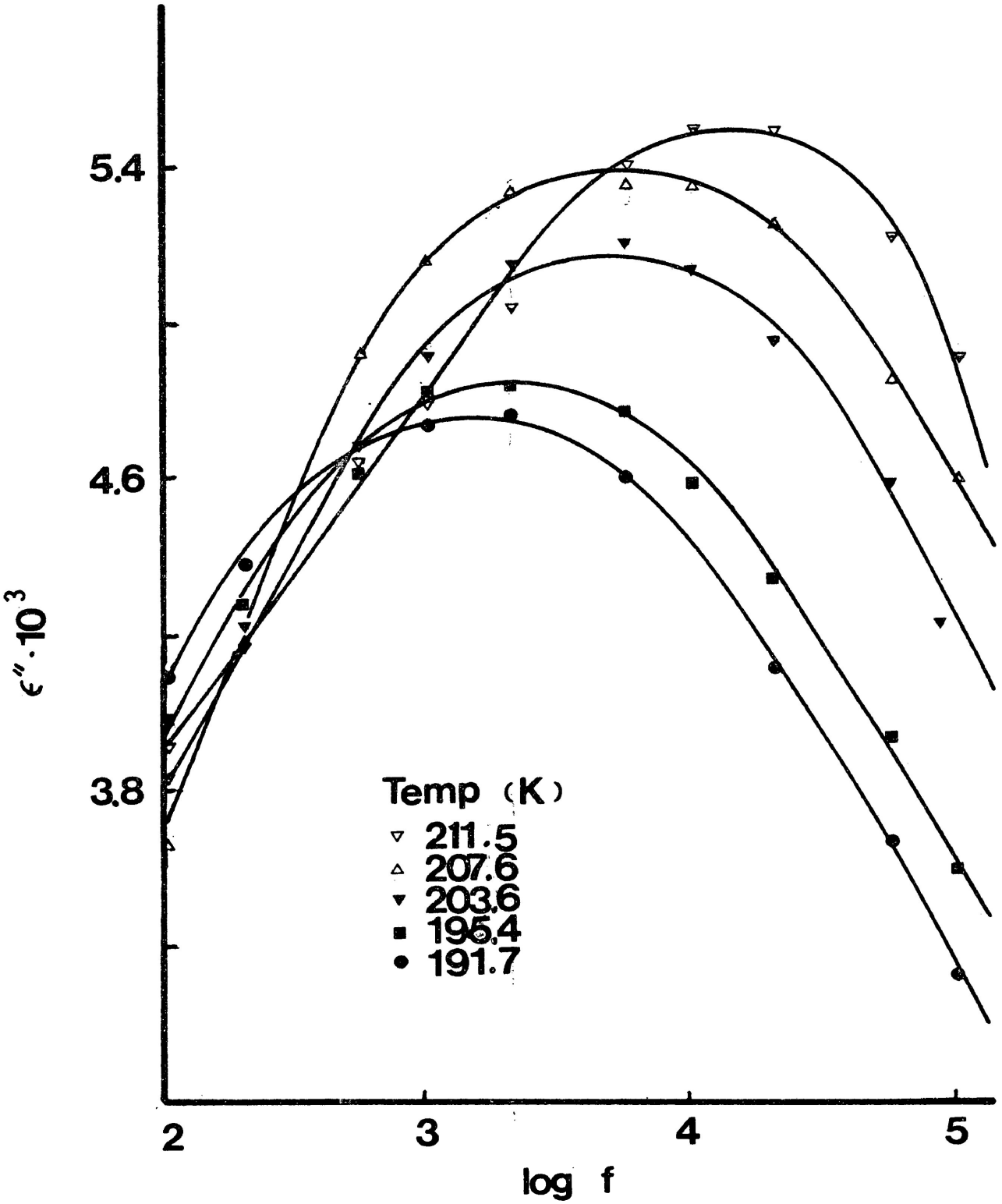


Figure V-12 Loss versus log frequency for p-bromoacetophenone (5% by weight in GOTP)

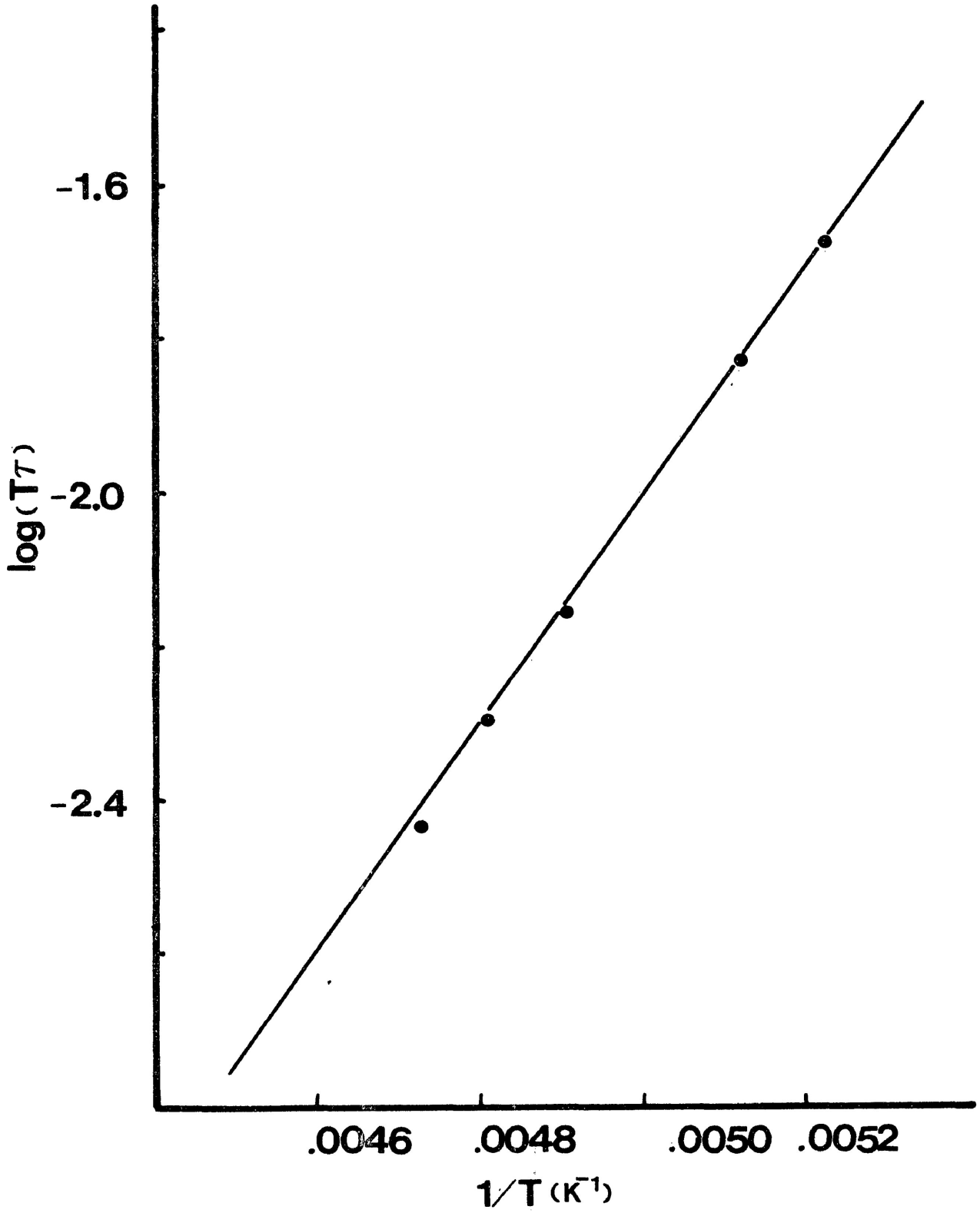


Figure V-13 Eyring plot for the previous set of loss curves for p-bromoacetophenone (5% by weight in GOTP

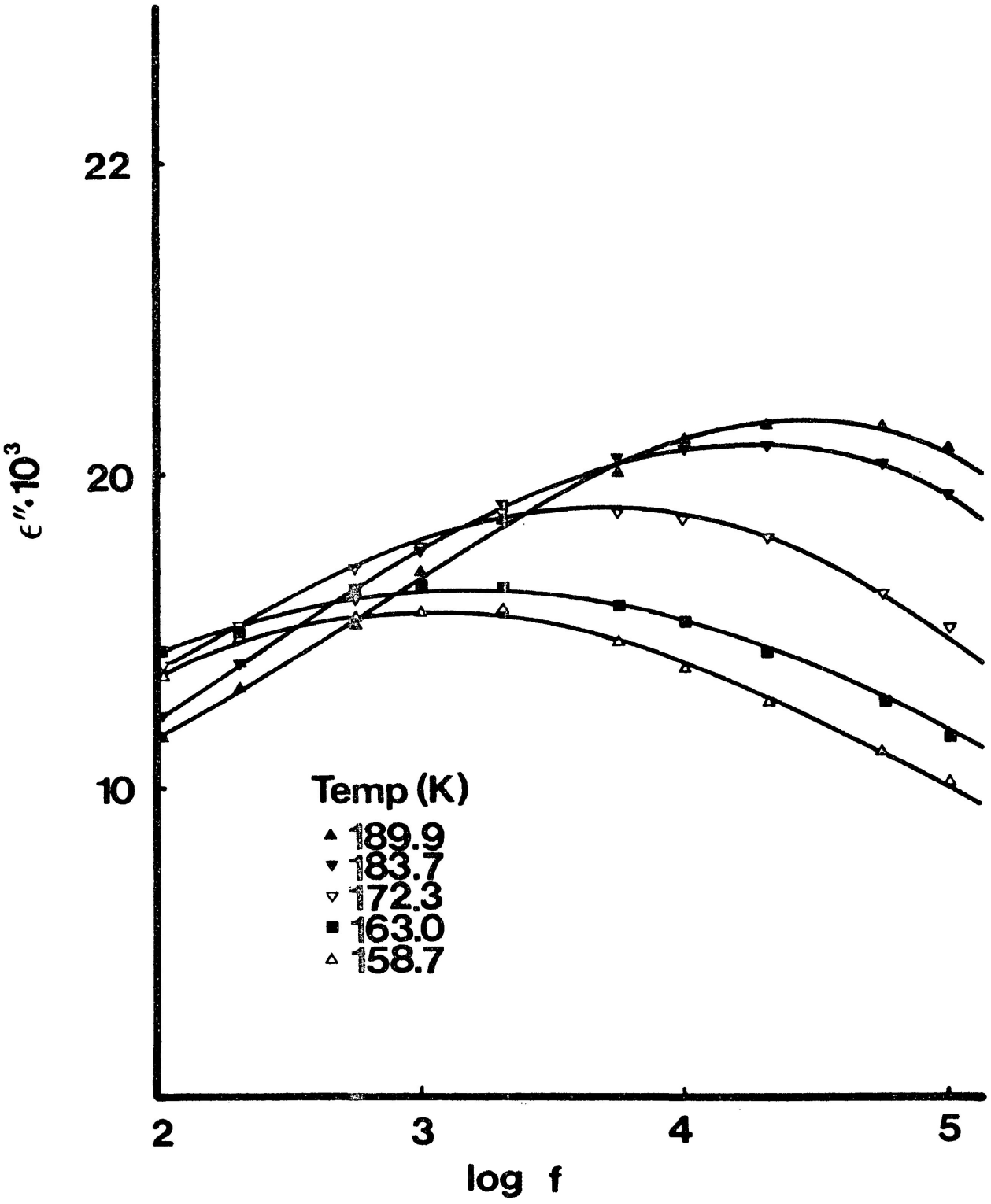


Figure V-14 Loss curves for the molecular process of 2-furaldehyde in GOTP. (5% solution by weight)

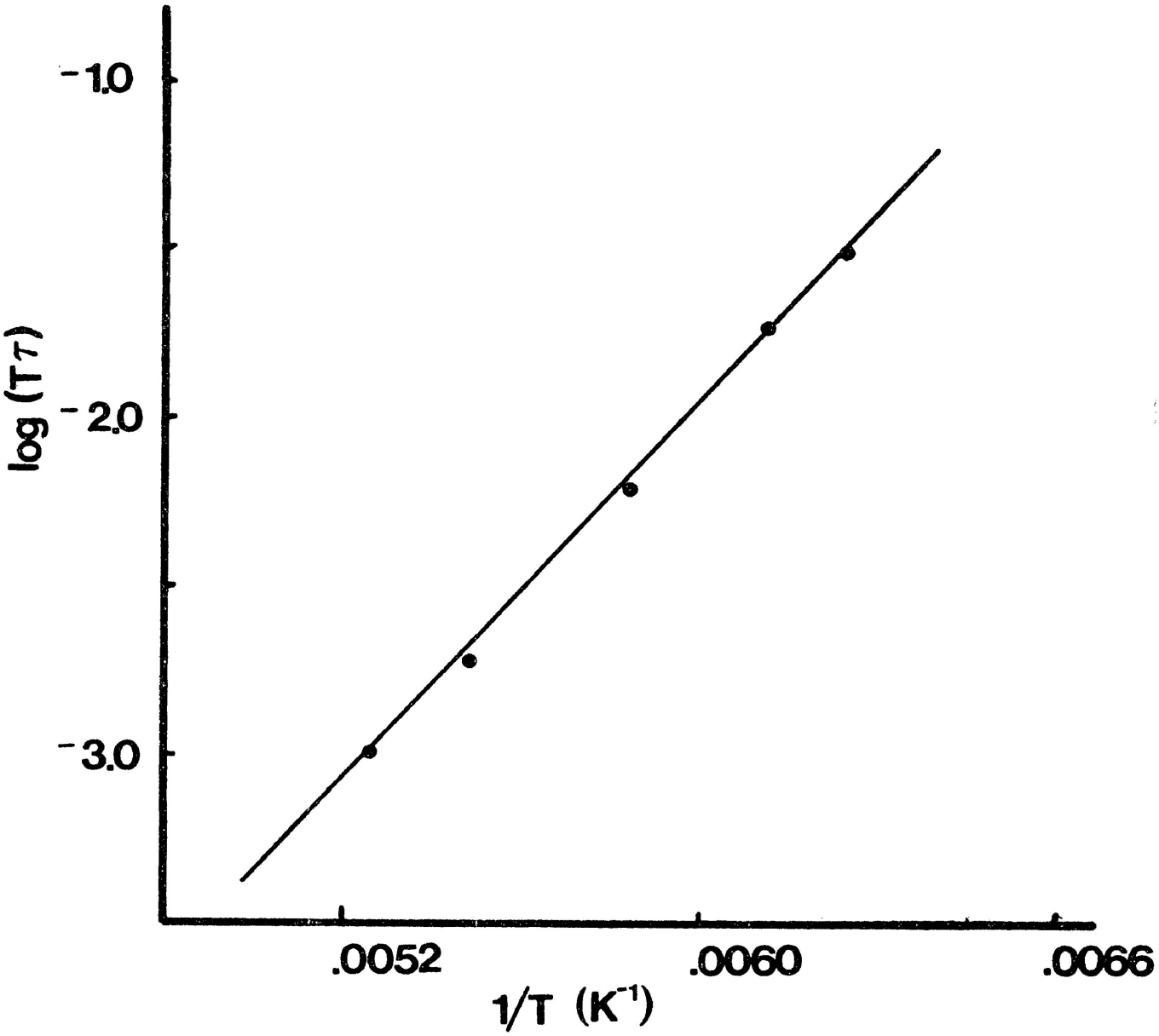


Figure V-15 Eyring curve for molecular process of 2-furaldehyde (5% in GOTP)

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C H A P T E R VI

CHARACTERIZATION OF INTRAMOLECULAR PROCESSES FOR A NUMBER OF BRIDGED DIARYL MOLECULES IN A VARIETY OF MEDIA

INTRODUCTION

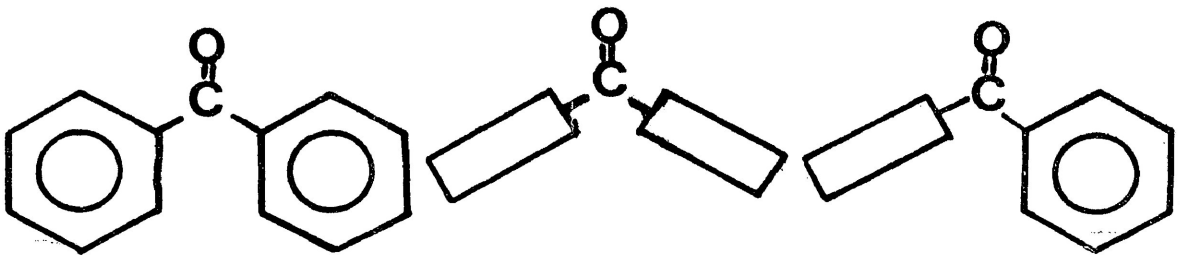
In 1949, E. Fisher [1] discovered that diphenyl ether has an anomolous dielectric relaxation behavior. A dielectric loss peak expected in the 5 cm wavelength region was not detected. Jackson and Powles [2], as well as Schneider [3], found that benzophenone, a molecule of similar size, shape, and net dipole moment orientation to diphenyl ether, behaved in this region as a rigid molecule.

A cursory comparison between diphenyl ether and benzophenone reveals a number of striking similarities. Firstly, the molar volume, as calculated for the rings of benzophenone and diphenyl ether in orthagonal configurations, (see later this chapter) are nearly identical: 170 cm^3 and 164 cm^3, respectively. Although the dipole moment for benzophenone is over twice that of diphenyl ether, both moments bisect the valency angle of the bridging groups. Dielectric studies on diphenyl ether have shown a major contribution from a very rapid intramolecular relaxation process which is different from straightforward phenoxy rotation whilst liquid solution studies in the microwave region indicate that there is a major

tion to the observed relaxation process.

More recently, other workers have found anomolous dielectric behavior in a variety of symmetric diaryl molecules including benzophenone, a molecule thought previously to relax as a predominantly rigid molecule, in a number of different solvent systems.

There has been some ambiguity in the literature with respect to the term 'symmetric diaryl molecules'. For the sake of simplicity, an idealized molecular orientation of the aryl components with respect to the bridging species is often taken. In this regard, benzophenone, which could adopt any one or combination of the orientations illustrated in Figure VI-1 has been thought of as a molecule with an orthogonal ring configuration as determined by methods such as x-ray diffraction studies. More recently, however, [4] experimental evidence indicates that the rings may not truly be orthogonal one to the other but rather have a phenyl-phenyl angle of some 60°. Regardless of the absolute orientation of these rings with respect to each other, it would seem safe to suggest that the orientation is somewhere between orthogonal and planar.



Sutton's Model Smyth's Model Morino's Model

Figure VI-1

A 'symmetric diaryl molecule' then is simply one in which the bridging species is attached to identically substituted aryl groups. How these groups ultimately orientate themselves (that factor which determines the actual symmetry of the molecule) is open to question. Figures VI-2 illustrates two possible conformations for these types of molecules. They were proposed by Sutton and Smyth, respectively. With the bridging species appropriately positioned on the y-axis and the aryl components positioned along the x-axis, there are two vertical planes of symmetry present, namely the y-z plane and the x-y plane.

In the past, these planes of symmetry have been a pre-requisite to the term 'symmetric diaryl molecule'. As previously stated, however, these idealized conditions need only be possible for the term to apply. Thus, benzophenone, diphenyl ether, and like bridged molecules are considered symmetrical regardless of the actual orientation

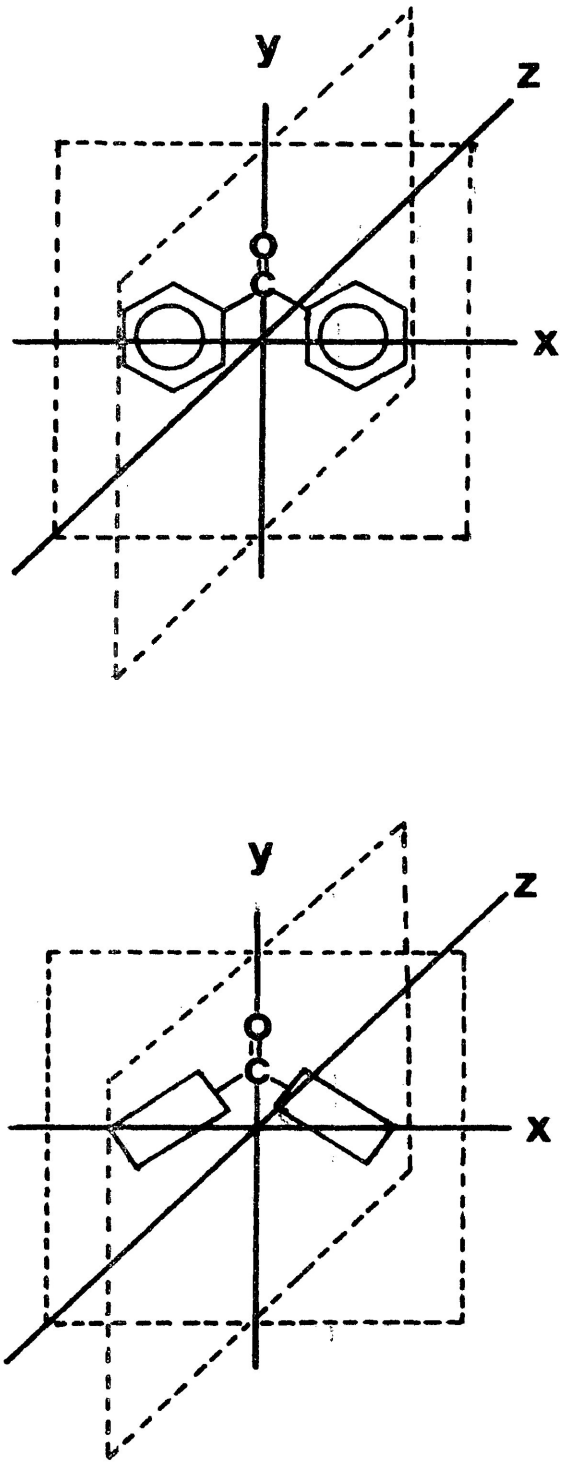
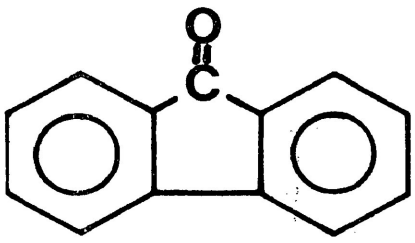


Figure VI-2 x-y, y-z symmetry for two configurations of benzophenone

adopted in space. Two other examples are p,p'-dimethyl phenyl ether and p,p'-dimethyl benzophenone.

Liquid solution studies of benzophenone in the microwave region [5] have shown that there is a major molecular contribution to the observed relaxation process.

Fischer [1] studied diphenyl ether in benzene solution at 296 K and observed a relaxation time of 2.9 ps. Benzophenone, however, was found to have a relaxation time of 20.4 ps. Fluorenone [6], a rigid planar molecule whose structure is given in Figure VI-3 has been studied by DiCarlo and Smyth [7] and shown to have a relaxation time of 19.9 ps. The striking similarity between the observed relaxation times for benzophenone and the planar molecule, fluorenone, would seem to indicate a more planar geometry in the former case than was previously imagined.



Fluorenone

Figure VI-3

Geometrical orientation, that is to say the position of the phenyl rings relative one to another in molecules of the bridged diphenyl type, has remained in some doubt in the past. Smyth and Walls [8] believed that the planes of the two rings were perpendicular to the plane of the bridging species valency angle. Sutton [9], however, stated that the two rings are in the plane of the bridging species valency angle resulting in a co-planar geometry. The Morino model [10], which suggests an orthogonal orientation of one ring to the other seemed to represent a reasonable compromise between these two. In fact, electron [11] and x-ray diffraction studies [12] of 2,2'-disubstituted ethers, along with proton n.m.r. [13] experiments, have established the orthogonal configuration of the rings one with the other. In the case of 4,4'-disubstituted ethers, and for this investigation more importantly, the ring orientations of benzophenone derivatives, the model which describes them may, in fact, be closer to Sutton's proposal of near coplanarity - that is to say some angle less than 90° between the two rings. Recent evidence has determined this angle to be of the order of 60° [4].

Benzophenone has been thought to be incapable

of intramolecular relaxation by a number of workers as the C-C carbonyl bond was thought to be too stiff [14]. While molecular relaxation processes have been observed for this molecule in cyclohexane at 298 K [15], it was felt that the Concerted Intramolecular Mechanism, as put forth by Fong, was not possible. Since the mesomeric moment of benzophenone is not appreciably different from acetophenone [16], the resonance effects in the two systems may reasonably be expected to be similar, and so benzophenone need not necessarily be rigid. Work carried out by this author indicates that there is, in fact, also a lower energy process associated with this molecule more than molecular relaxation itself. (see later this chapter)

Diphenyl ether, for example, has a relaxation time in benzene of 1/5 to 1/6 that of benzophenone in the same system, while in the more viscous solvent Nujol [9] the relaxation time is 1/50 that of benzophenone [2]. It has been suggested that the shorter value of τ for diphenyl ether, as compared to a similarly sized molecule such as benzophenone, may be attributed to internal rotation of both phenyl rings [8]. By this reasoning a fixed volume would be swept out during the rotation. From

Debye theory, it becomes difficult to explain the ratio of the rotating volume of diphenyl ether to benzophenone in Nujol as 2% as compared to 22% in benzene. Some internal, less volume-dependent motion must therefore be responsible for the rapid relaxation process. Further evidence to this end is that both pyridine, τ=5.6 ps, at 298 K, and fluorobenzene, τ=8.4 ps, at 293 K, each studied in benzene [17], have longer relaxation times than diphenyl ether although they are most certainly much smaller molecules, and, in fact, each is similar in size and shape to one of the bridging phenyl rings. Clearly, some low energy mechanism is at work in the relaxation process as observed for these symmetrical molecules. Subsequent experimental evidence indicates that absolute molecular symmetry is not a fundamental requirement to this observed anomalously low energy relaxation process.

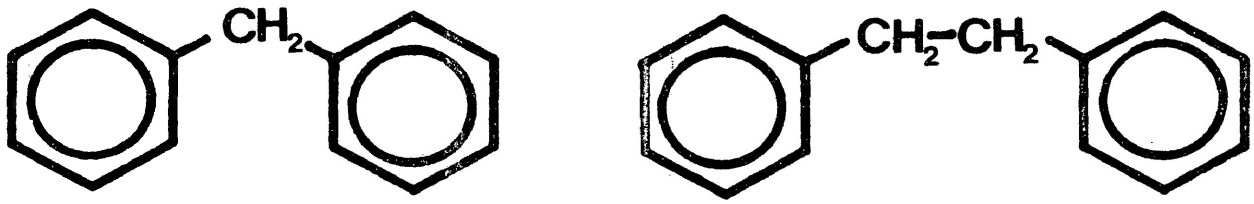
In effect, a number of mechanisms has been put forward to explain what would appear to be anomalously short relaxation times (and consequently, low enthalpies of activation, ΔH_E (kJ mol^{-1}), for processes associated with symmetrical diaryl molecules). These include inversion [1], atomic dipole reversal [18], phenoxy group rotation [19], mechanical double-internal rotation [14], and

mesomeric shift of charge [20].

Inversion would require a large change in the position of carbon atoms, and since the force constant of the ether linkage (in the case of diaryl ethers) is significant, this is highly improbable. It becomes even less likely in the case of benzophenone.

The atomic dipole reversal mechanism was proposed by Fisher [1] who considered that the atomic dipole moment due to the oxygen lone pair of electrons is modified by resonance with the phenyl rings. As the phenyl rings rotate about their bonds to the oxygen atom, they move into orientations which permit more or less resonance and thus change both the magnitude and then ultimately the direction of the atomic dipole moment. While these ring rotations might be responsible for the short relaxation times observed in the symmetric diaryl molecules of the bridge types, it could not explain the reduced relaxation times of 6.5 and 13.3 ps for diphenylmethane and bibenzyl respectively, as these molecules have no lone-pair electrons available to interact with the π-cloud electrons of the adjacent phenyl rings.

It may be possible that broad band absorption, characteristic of organic molecules of this type, plays a role in this process. (see Figure VI-4 for the structures of these molecules).



Diphenylmethane Bibenzyl

Figure VI-4

Phenoxy rotation alone cannot account for the relaxation processes observed in symmetric diaryl molecules. In order to conserve angular momentum, so that the location of the centre of mass of the molecule does not change, the rotation of a phenoxy group with respect to the phenyl ring requires a comparable displacement of each ring unless one ring is held fixed in plane by external forces. In fact, when both rings

move in the concerted fashion previously described, the double internal rotation mechanism (c.f. CIM) may be evoked. The following Figure VI-5 diagramatically presents this concept.

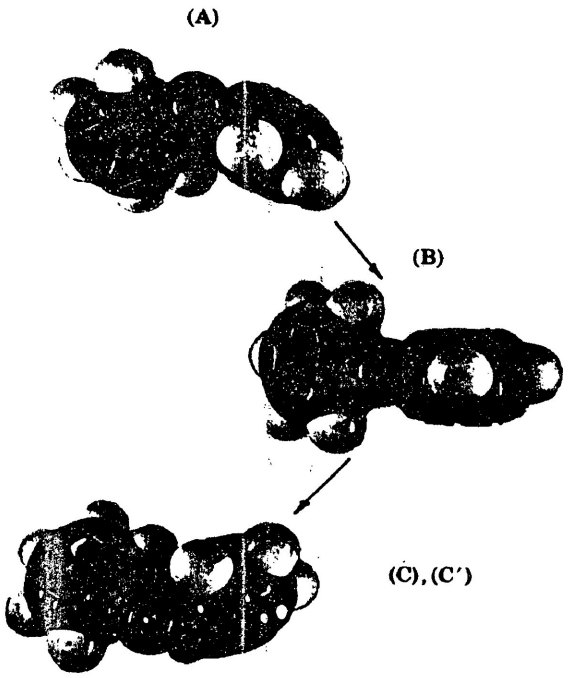


Figure VI-5 The concerted intramolecular rotation in diphenyl ether. An elementary step in the relaxation process presumably involves a transition from one equilibrium configuration (*a*) to another (*c*).

The final mechanism to be discussed in this chapter is that of the mesomeric moment shift. Through the interaction of the π-electrons of the phenyl rings with the unshared electron pairs on the bridging atom, there is a shift of charge and a concomitant shift of dipole moment. The maximum value of the mesomeric moment arises when p-orbitals of the ring which is co-planar with the oxygen valency angle have a maximum over-lap with the appropriate p-orbital of the oxygen atom.

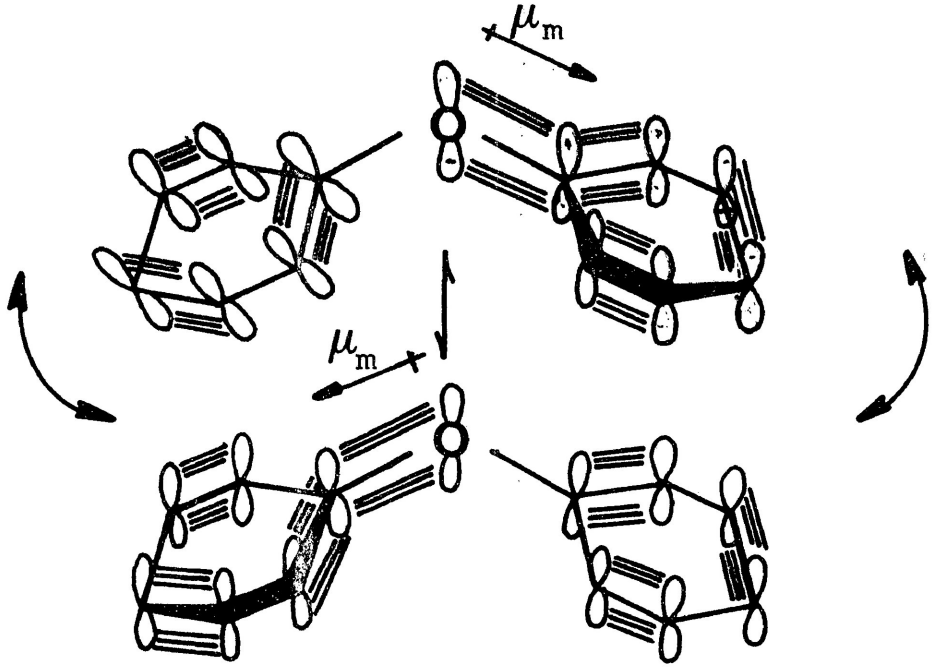


Figure VI-6 Mesomeric moment mechanism showing possible p-orbital overlap.

From Figure VI-6, it may be seen that as the p-orbitals of the phenyl ring come into a perpendicular orientation with respect to the available p-orbital on the bridging atom, the resulting mesomeric moment increases. Similarly, the other phenyl ring follows a like path, (since these rings are assumed to maintain ultimately an equilibrium orientation with respect to each other) so the mesomeric moment reverses direction.

To date, the mesomeric moment and concerted intramolecular motion (CIM) mechanisms have been considered the most probable mechanisms for this low energy intramolecular process.

The major difficulty with the mesomeric moment mechanism is the need for apparently unreasonably large dipole moments resulting from these π-cloud interactions.

Vaughan et al [21], in a theoretical treatment of the experimental dielectric absorption observed with pure liquid diphenyl ether, have indicated that the mesomeric values required need not be greater than $\sim$1.8 D

and that the observed dielectric characteristics could not be explained in terms of a concerted intramolecular motion in any regard. This is the first theoretical indication that the mesomeric moment required for a low energy intramolecular process in this type of molecule need not be unreasonably large.

There has been indirect evidence in the literature to the effect that benzophenone exhibits an intramolecular process. For many years, the precise nature of this process has remained uncertain.

Desando [22] has studied a large number of symmetrical diaryl bridged molecules showing similar anomalously short relaxation times in polystyrene. In order to explore the symmetric constraint placed on the concerted intramolecular relaxation process (CIM) proposed by Fong, and indirectly to test the mesomeric moment mechanism, a subtly asymmetric, bridged diaryl molecule has been studied recently. The results of these studies are presented in the Experimental Results section of this chapter.

One difficulty in comparing symmetric and

asymmetric molecules of this type has been in determining the effect of the asymmetric component on the observed relaxation process. Clearly, there are substantial differences between benzophenone and say p-bromobenzophenone. Likewise, 2-benzoylpyridine differs only slightly from benzophenone in terms of molecular weight but the presence of the nitrogen lone electrons, and the associated dipole moment direction, may alter the relaxation characteristics substantially.

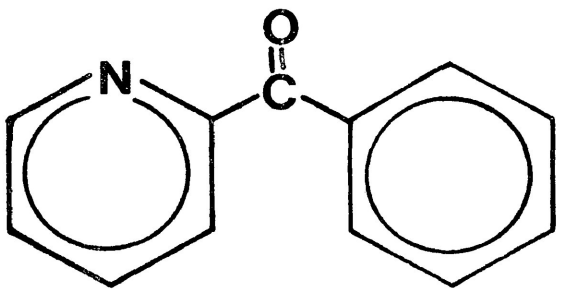


Figure VI-7 2-Benzoyl pyridine

With this in mind, an analogue of benzophenone has been synthesized which physically and electronically is virtually identical to the parent molecule. The synthesis of this isotopic analogue, 2,3,4,5,6-pentadeuterobenzophenone has been detailed in the experimental section,

Chapter III. The most significant aspect of this molecule is that its centre of mass, unlike that of benzophenone, which has its centre of mass located along the axis of symmetry passing through the carbonyl group and somewhat below the bridging species, has been displaced from that axis toward the deuterated phenyl ring (see Figure VI-8).

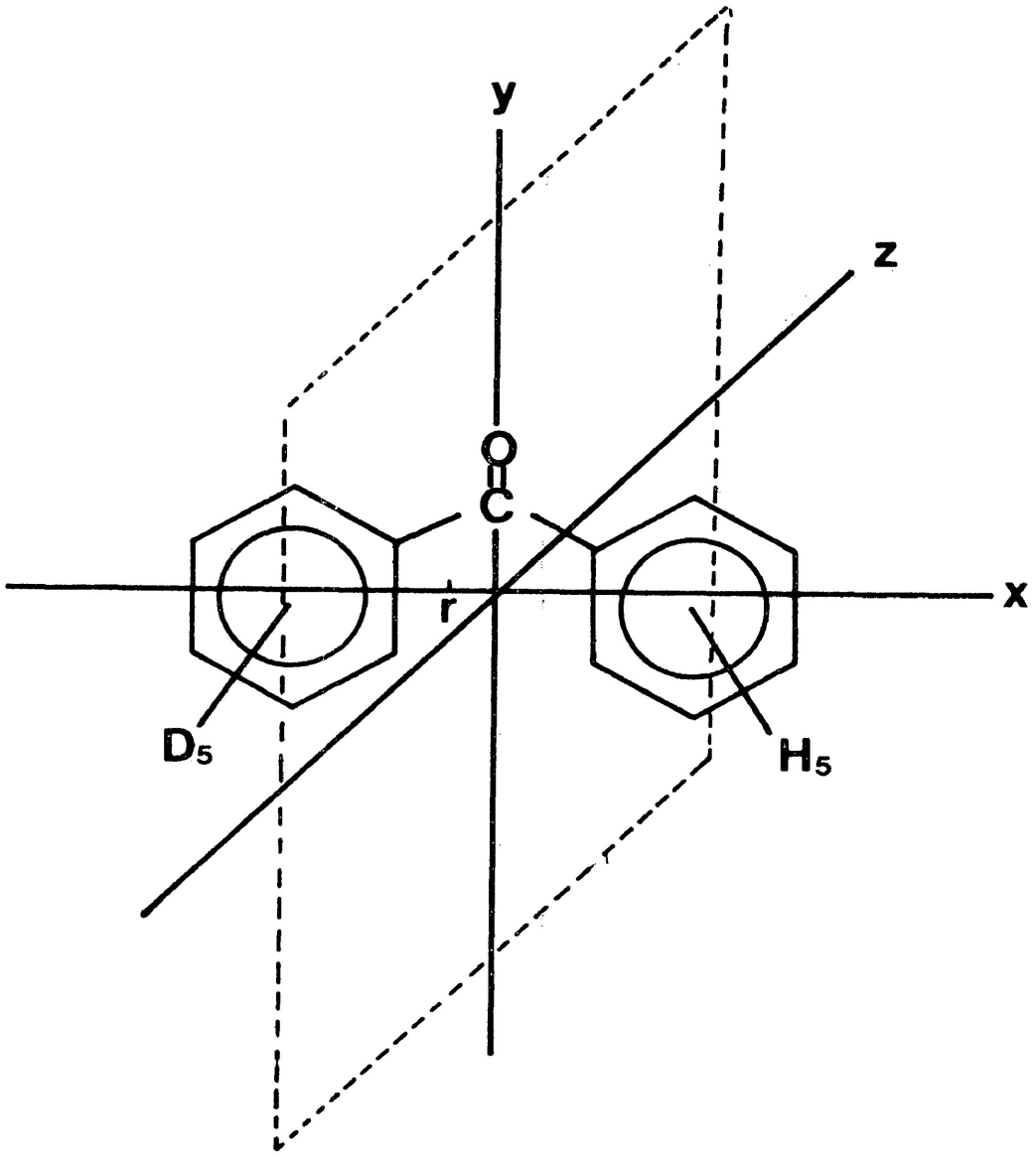
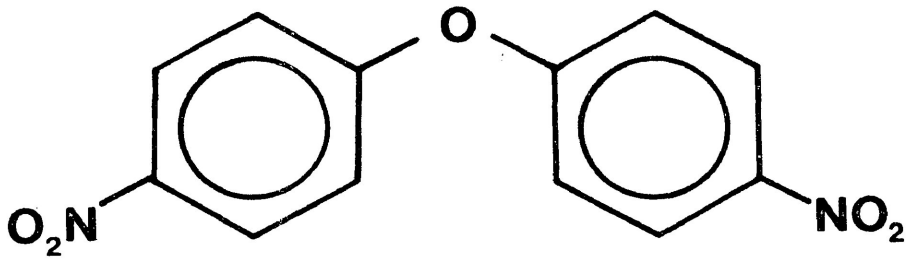


Figure VI-8 Centre of mass shift in benzophenone-d_5

In this case then, similar dielectric behavior by the deuterium analogue would make the CIM mechanism untenable.

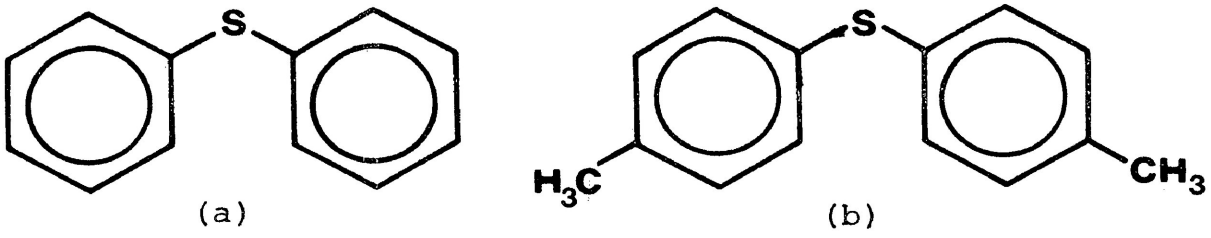
It is the purpose of this chapter to clearly establish the presence of a low energy dielectric relaxation process for benzophenone and related molecules. In one substituted bridged diaryl molecule, studied by this author, namely bis(p-nitrophenyl) ether, examined in atactic polystyrene, both the molecular and intramolecular processes have been observed in the same sample



bis(p-nitrophenyl)ether

Figure VI-9

As well, the molecular relaxation processes for diphenyl sulfide and bis(p-tolyl)sulfide in polystyrene have been determined. Other data for rigid molecules of comparable size has been gleaned from the literature and presented as required. In the cases of diphenyl sulfide and p-tolylsulfide studied in polystyrene, the intramolecular processes have already been determined by Desando [22] of this laboratory. The structures of these molecules are given below as Figure VI-10.



(a) (b)

Figure VI-10

a) diphenyl sulfide
b) bis(p-tolyl)sulfide

Clearly, certain flexible molecules studied in given media present both molecular and intramolecular processes that are well separated and defined in terms of their Eyring parameters. Several cases have already been mentioned. Unfortunately, molecular and intramolecular processes in flexible molecules are not always simultaneously observed. This may be a result of a number of factors. With certain molecules, one or both of the molecular or intramolecular absorption curves will be above or below the usable range of the solvent system chosen. In cases where only one process is observed the type of process, that is to say whether it is molecular or intramolecular in nature, can often be determined by the magnitude of the enthalpy of activation and the temperature region over which the absorption curves are found relative to those of rigid molecules of similar size and shape.

In some cases, however, molecular and intramolecular relaxation processes occur in virtually the same temperature/frequency regions for a given molecule. When this occurs, it becomes a rather difficult task to ascribe (with any degree of certanty) accurate Eyring

parameters to these complex absorption processes. Methods of treating such data have been discussed in previous chapters (cf. Chapter II). In certain cases (cf. Chapter V) the consequences of molecular and intramolecular overlap can be shown to alter little the actual position of the frequency maximum for the process under study; howevever, the ultimate accuracy of the calculated Eyring parameters, i.e. ΔH_E, ΔS_E etc., may certainly fall into question. The net effect is a general broadening of the observed dielectric dispersion, particularly when the process under study exhibits low dielectric loss maxima (see discussion later this chapter).

With all these facts in mind, and the historical perspective provided in the literature carefully weighed, the results of the study of a number of symmetric and asymmetric diaryl molecules are presented and discussed in the following sections. When possible, reported studies of relevant molecules by other authors are presented for comparison. While these studies have largely been carried out in three different media, they are not in themselves studies of media effects.

EXPERIMENTAL RESULTS

All molecules studied by this author were commercially prepared with the exceptions of 2,3,4,5,6-pentadeuterobenzophenone, bis(p-nitrophenyl)ether and bis(p-toly)sulfide. These were synthesized by the author, J. Chao, and M.A. Desando, respectively. As well, certain references will be made to rigid molecules studied by other authors as required.

Inasmuch as the central focus of this chapter is the study of benzophenone and its deuterated analogue in a variety of media, these data are presented in Table VI-1. The para-halo-substituted molecule, p-bromo-benzophenone, has also been studied and is, for convenience, included in this table. Tables VI-2 and -3 are summaries of the Eyring parameters determined for diaryl thioethers and diaryl ether molecules, respectively, studied in the solvents indicated. Again, a molecule related to the diaryl ethers, namely p-methylanisole, has been included in Table VI-3. Table VI-4 provides data for two representative rigid molecules of comparable size to those flexible molecules studied here.

TABLE VI-1

Flexible Diaryl Molecules in various Media

SOLVENT	TEMPERATURE RANGE (K)	Log f_{max}	$\bar{\beta}$	$\Delta G_{200\ K}$ (kJ mol^{-1})	$\tau_{200\ K}$ (S)	ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1}mol^{-1})
				Benzophenone			
GOTP	155-194	2.52-4.21	0.18	29.6	7.2×10^{-6}	22 ±3	-31 ±14
Santovac	149-199	2.32-4.47	0.20	28.1	5.16×10^{-6}	23 ±3	-25 ±10
P.S.	135-194	2.78-4.95	0.18	25.4	1.01×10^{-6}	18 ±3	-35 ±14
				2,3,4,5,6-Pentadeuterobenzophenone			
GOTP	144-213	1.98-3.80	0.17	31.7	4.58×10^{-5}	14 ±3	-67 ± 7
Santovac	142-183	1.93-3.85	0.18	28.9	8.59×10^{-6}	21 ±3	-39 ±12
P.S.	151-221	2.82-4.46	0.17	29.7	1.36×10^{-5}	15 ±3	-74 ±19
				p-Bromobenzophenone			
GOTP	215-231	3.21-4.10	0.39	36.9	1.08×10^{-3}	32 ±4	-27 ±19

TABLE VI-2

SOLVENT	TEMPERATURE RANGE (K)	Log f_{max}		$\Delta G_{200\ K}$ (kJ mol^{-1})	$\tau_{200\ K}$ (S)	ΔH_E (kJ mol^{-1})	ΔS_E (J $K^{-1} mol^{-1}$)
				bis(p-nitrophenyl)ether			
P.S.	171-199	1.68-4.36	0.19	26.1	1.58×10^{-6}	71 ±9	224 ±47
	97-125	3.08-4.10	0.15	24.1	4.60×10^{-7}	8 ±3	-82 ±13
				p-methylanisole			
GOTP	81-106	3.05-4.31	0.32	21.0	7.30×10^{-7}	7 ±3	-68 ±14

TABLE VI-3

				diphenyl sulfide			
P.S.	207-231	3.12-4.92	0.34	35.5	4.35×10^{-4}	66 ±5	154 ±23
				bis(p-tolyl) sulfide			
P.S.	192-203	3.00-4.01	0.35	31.4	3.07×10^{-5}	69 ±9	191 ±38

TABLE VI-4

MOLECULE	T(K)	τ(s) 200 K	ΔG_E (kJ mol^{-1}) 200 K	ΔH_E (kJ mol^{-1})	ΔS_E (J K^{-1} mol^{-1})
o-hydroxy-benzophenone (23)	256-294	3.7×10^{-1}	47	58 ±3	58 ±4
diphenyl-sulfone (22)	205-240	1.7×10^{-3}	48	60 ±4	60 ±15

Table VI-4 presents the Eyring parameters for two rigid molecules of similar size to those flexible molecules presented in this chapter.

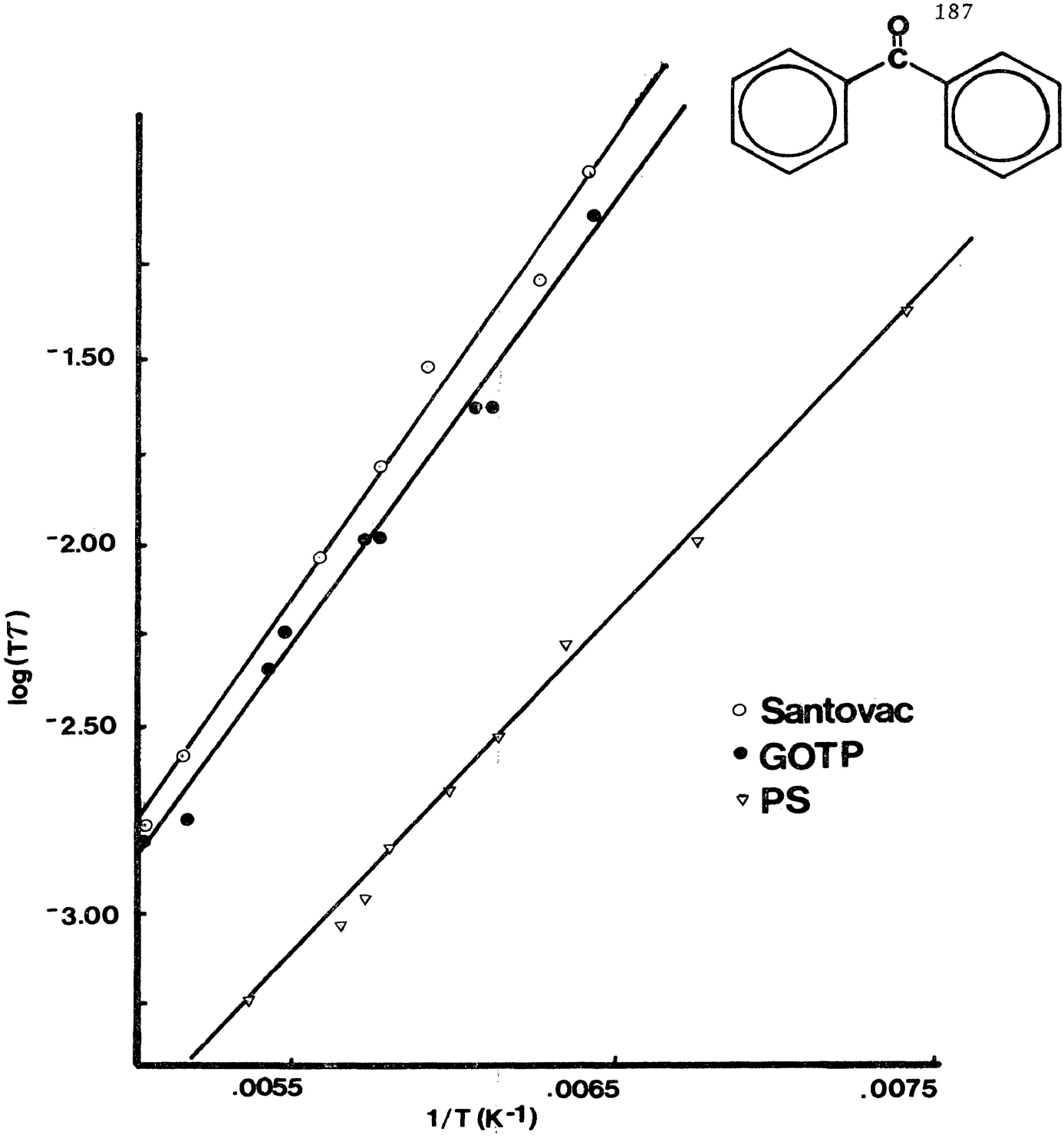


Figure VI-11 Eyring plots for benzophenone as studied in three media

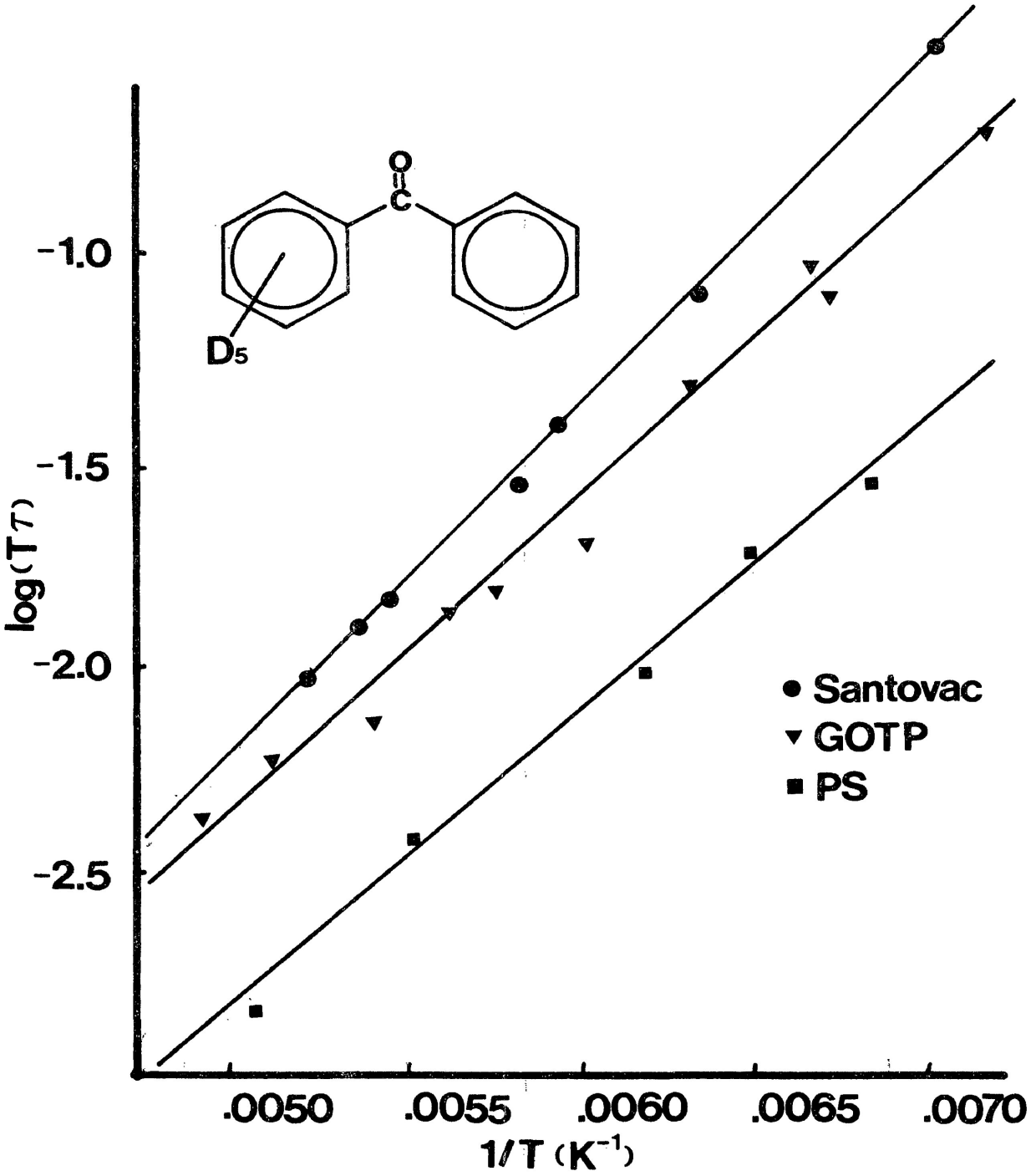


Figure VI-12 Eyring plots for D_5-benzophenone as studied in three media

DISCUSSION

A number of interesting results have been observed in the study of flexible bridged diaryl molecules in several solvents. Benzophenone, as studied in polystyrene, glassy o-terphenyl, and Santovac solutions of relatively low concentrations (i.e. <8% solute by weight) has clearly shown on comparison with similarly sized rigid molecules, what must be considered an intramolecular relaxation process.

Table VI-1 presents the results of the study of this molecule in three media. Several interesting points should be made. Firstly, the Eyring parameters for benzophenone studied in these solvents all agree, within experimental error, with each other. From Figure VI-11, which is a plot of the Eyring analysis of this molecule, it may be seen that reasonably linear correlations exist within the data. If this is compared with Figure VI-12, the Eyring Analysis of the deuterated analogue in the same solvents, it should be noted that the relative positions of the curves are the same for both solutes. This implies two things, (1) that while absolute enthalpy values may vary between solvents, they are relatively the same, and

(2) that again, within experimental error, the entropy affects observed for both the parent molecule and its deuterated analogue in the three systems seem to be consistent between solvents.

It must also be noted that for each of these molecules, the observed processes occurred in each solvent over virtually identical temperature and frequency ranges. The Eyring data clearly supports the premise that both molecules are relaxing through a common mechanism.

Confirmation of the identity of this process, that is to say whether the evidence is consistent with a molecular or an intramolecular process, is quite simple on account of two facts: the magnitude of loss observed for these molecules is much lower than that expected for molecular relaxation in a dipole with the magnitude of benzophenone ($\mu \sim 3D$) in the concentrations used. As well, the molecular relaxation process for a similar sized rigid molecule, diphenyl sulfone studied in polystyrene [24], has a ΔH_E value considerably higher than that observed in this case.

The molecule, o-hydroxybenzophenone, studied in polystyrene [23] is of similar size to benzophenone, and, although the hydroxyl group which hydrogen bonds to the carbonyl oxygen changes the magnitude of the dipole moment along the vertical axis slightly, i.e. that component parallel to the carbonyl group, this does not alter the net dipole moment of the molecule appreciably. Steric constraints limit the motion of the other phenyl ring. Thus, the molecule is rigid. This molecule, also studied at similar concentrations in polystyrene, exhibited loss values at much higher temperatures which are an order of magnitude greater than that observed in the case of benzophenone in polystyrene at slightly lower concentrations. This implies that the magnitudes of the relaxing dipoles are less in the lower temperature process observed for benzophenone.

If we compare enthalpies of activation for rigid molecules of similar size to benzophenone, we can see that these molecules all have ΔH_E (kJ mol^{-1}) values far in excess of those observed for the low temperature process in benzophenone in the same

solvent system. Table VI-4 presents the Eyring parameters for two of these rigid molecules.

Both of these rigid molecules have similar Eyring parameters which, when compared to the results in Table VI-1, support the idea that the processes detected in benzophenone and 2,3,4,5,6-pentadeutero-benzophenone are intramolecular in origin.

From this evidence certain mechanistic comments may be made. Assuming, in fact, that both benzophenone and 2,3,4,5,6-pentadeuterobenzophenone relax by the same mechanism, in view of the magnitude of the observed loss being considerably less than that expected for a relaxing carbonyl group, it would seem that an alternate dipole is involved in the dielectric dispersions observed in these molecules. Further to this, the centre of mass of the benzophenone analogue has been shifted toward the pentadeutero ring. Since a prerequisite to one of the most popular mechanisms used to account for dielectric behavior in symmetric bridged diaryl molecules (the CIM mechanism) is conservation of angular momentum, and to quote, "...provided that the centre of gravity of the molecule

is kept invariant" [25], also inasmuch as this is not possible in the pentadeutero analogue, double internal rotation would seem untenable in both the cases of benzophenone and 2,3,4,5,6-pentadeuterobenzophenone as studied in the three previously described solvents by this author. Relaxation through the mesomeric moment mechanism is, however, quite possible.

Clearly the question has always been whether or not the magnitude of the mesomeric moment of such molecules is great enough to exhibit a detectable relaxation process. Current evidence in both a theoretical and an experimental sense has suggested that the mesomeric moments generated in molecules such as benzophenone are, in fact, large enough to account for the observed dielectric phenomena for bridged diaryl molecules of the type previously discussed.

Vaughan [21] has suggested that from a theoretical treatment of the experimental results observed for diphenyl ether, a much better account of the observed dielectric absorption is possible by

considering the mesomeric moment mechanism. His work maintains that for diphenyl ether, a maximum mesomeric moment of no greater than that proposed by Higasi need be required [25]. Higasi suggests a limiting value of approximately 1.81 D at 313 K.

In order to determine the accuracy of the Eyring parameters calculated, particularly from quite broad loss curves, ($\overline{\beta}$ <0.2), the possibility of molecular overlap was considered. Generally, when one speaks of two overlapping processes, it is in reference to the overlap of molecular and intramolecular maxima. As has been previously stated, researchers have searched for solute-solvent systems which best separate the positions of the observed loss maxima for the molecular and intramolecular processes, respectively. In the cases where the magnitude of the loss is low i.e. $\varepsilon'' < 1 \times 10^{-2}$, it may be necessary to consider the tail end contribution of other processes considerably well removed from the temperature/frequency range where the absorption maxima of interest occurs.

It was with this in mind that curves of loss versus temperature at two fixed frequencies were studied in glassy o-terphenyl for the limiting geometric orientations possible for benzophenone. As well, similar curves were obtained for these molecules in the solvent, Santovac®. From Figures VI-15 and -16, one can see that the molecular contribution from these limiting cases is even less in magnitude. The two molecules chosen were o-hydroxybenzophenone, which represents the most orthogonal configuration possible, and fluorenone, which is a planar molecule. The startling fact is that at temperatures where the intramolecular process of benzophenone is found, both fluorenone and o-hydroxybenzophenone have loss values of the order of magnitude of that observed for benzophenone in glassy o-terphenyl in the case of the o-hydroxybenzophenone and, in the case of fluorenone, more than an order of magnitude greater, for systems all of the same relative solute-solvent weight concentrations. Thus, in cases where low loss solutes are involved, researchers ought not to dismiss the possible tail end contributions of processes considered to be far removed from the process under study (see

Figures VI-13, -14, -15 and -16).

Figures VI-17, -18, and -19 are the dielectric loss versus logf curves for benzophenone in glassy o-terphenyl, Santovac, and polystyrene, respectively. Figures VI-20, -21, and -22 are the corresponding curves for the pentadeuterobenzophenone in the same solvents. It is important to note that these curves are plots of corrected dielectric loss; that is to say that experimental data points which did not fall on the 'best fit' of the bulk of the data to the Fuoss-Kirkwood equation were calculated by curvilinear regression within the computer program. All curves presented, however, had correlation coefficients, r^2 in excess of 0.9600 for the uncorrected loss data.

p-Bromobenzophenone has also been studied in glassy o-terphenyl, the results of which are presented in Table VI-1. The temperature region over which this process has been observed is 215 to 231 K which is some 30 K higher than the region in which benzophenone and its pentadeuterated analogue seem to relax. As well, the free energy of activation at 200 K for this process is considerably larger

than that observed for the two molecules previously mentioned. The values for benzophenone and its analogue are, at 200 K, 28.6 and 31.7 kJ mol^{-1}, respectively, while the value for p-bromobenzophenone at the same temperature is 36.9 kJ mol^{-1}.

On comparison of other Eyring parameters, the likelihood of a different process at work in p-bromobenzophenone becomes even more apparent. The enthalpies of activation for benzophenone and its analogue are of the same order, $\sim$18 kJ mol^{-1} when studied in glassy o-terphenyl while the enthalpy of activation for p-bromobenzophenone in this medium is considerably higher, 32 ±4 kJ mol^{-1}. The entropy values do not differ dramatically. Perhaps even more striking are the relaxation times at 200 K for these three molecules. p-Bromobenzophenone has a τ value some three orders of magnitude greater than those values observed in benzophenone and pentadeuterobenzophenone at the same temperature. (p-bromobenzophenone - $\tau_{200\ K} = 7.21 \times 10^{-6}$ s, and 2,3,4,5,6-pentadeuterobenzophenone - $\tau_{200\ K} = 4.5 \times 10^{-5}$).

M. A. Desando has studied a molecule which can

reasonably be compared to p-bromobenzophenone. This molecule, 4-biphenylyl phenyl ether has, in polystyrene, shown a dielectric process with similar Eyring behavior to that of the bromo ketone. The $\tau_{200\ K}$ of $2x10^{-4}$ s and ΔG_E at 200 K of 34.1 tend to suggest that the process being observed in the bromo ketone is likely simple benzoyl group relaxation about the p-bromophenyl carbon - carbonyl carbon bond. The enthalpy of activation in the 4-biphenylyl phenyl ketone is considerably smaller than that observed in the benzoyl group relaxation 16.6 kJ mol^{-1} ±3 [17] in the former and 32 ±4 kJ mol^{-1} in the latter, but then one would reasonably expect a 'stiffer' bond character in the carbon - carbon bond of the carbonyl compound as compared to the 'stiffness' of the carbon-oxygen bond in the ether. The loss versus log frequency curves for the bromo ketone is presented as Figure VI-23.

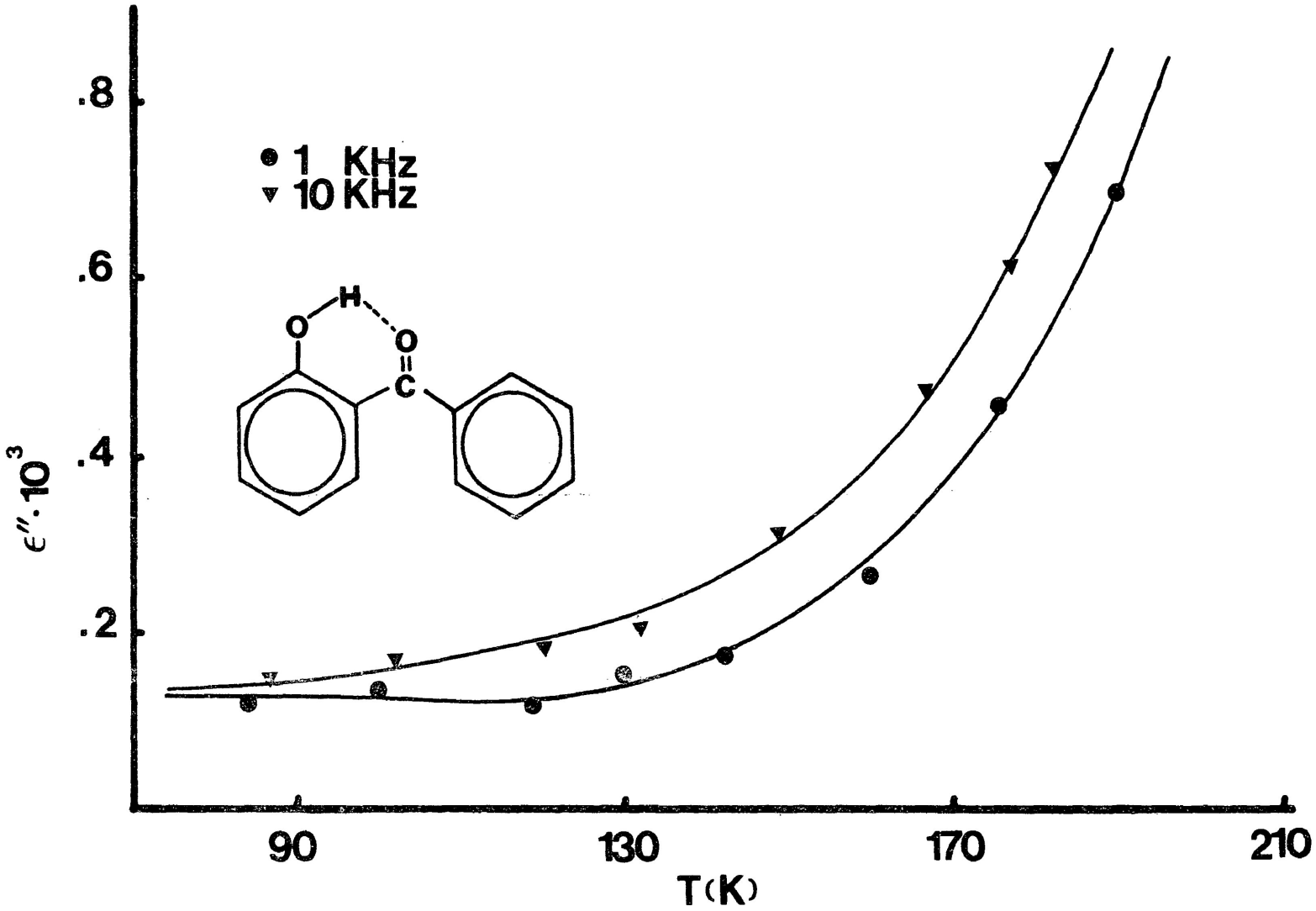


Figure VI-13 Dielectric loss plotted against temperature for the orthogonal limit of benzophenone, 5% o-hydroxybenzophone in GOTP

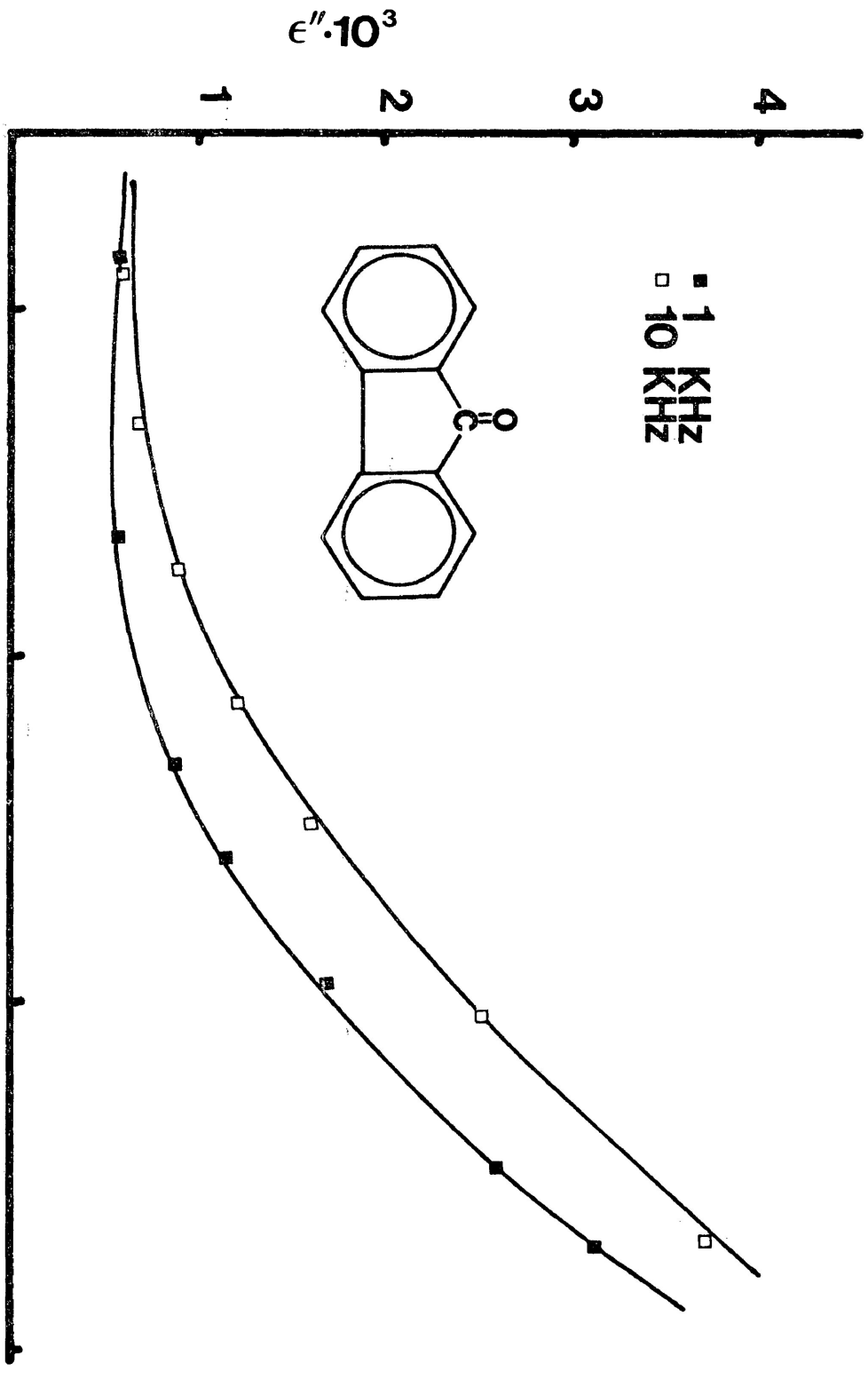


Figure VI-14 Dielectric loss plotted against temperature for the

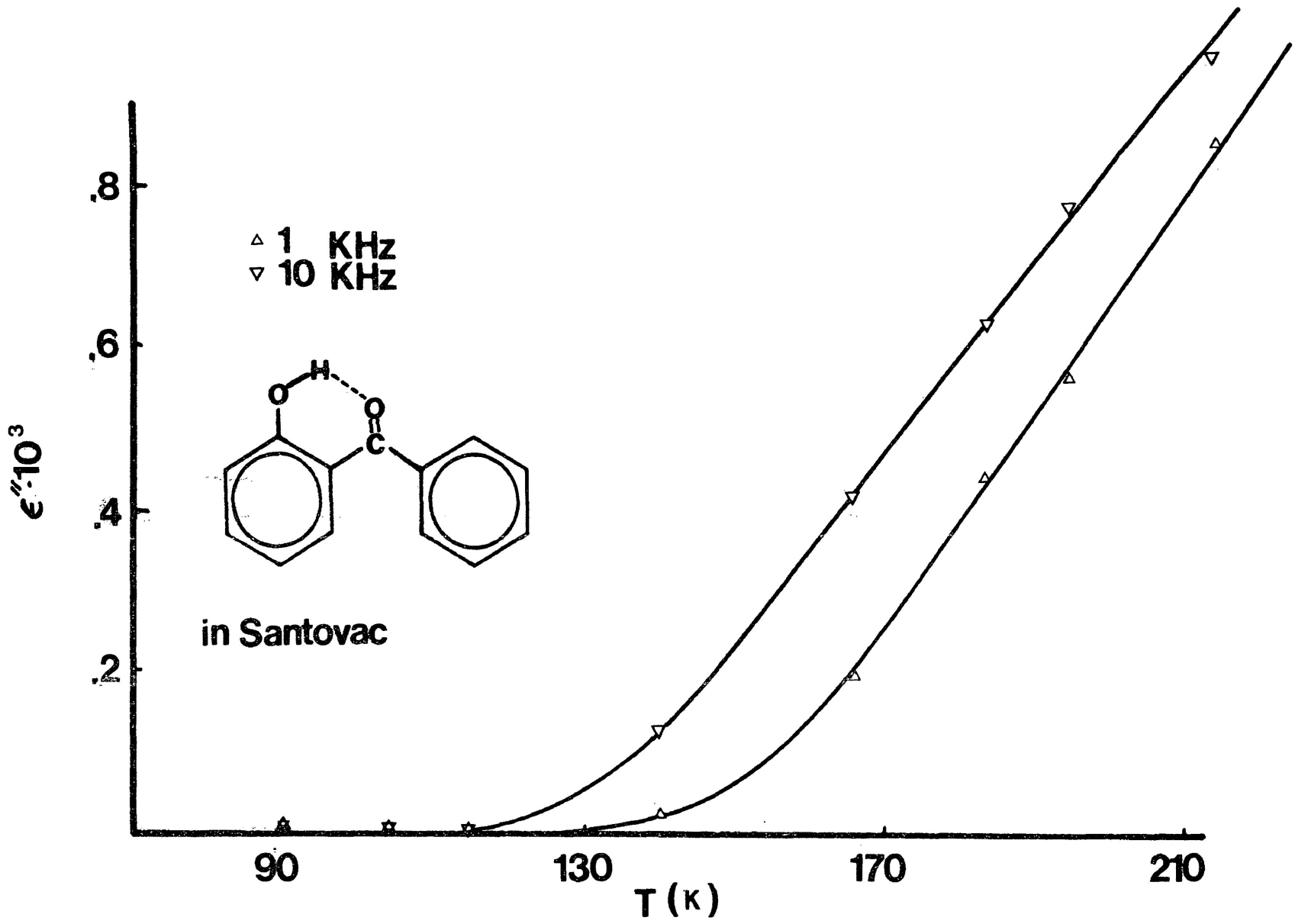


Figure VI-15 Dielectric loss plotted against temperature for o-hydroxybenzophenone at 5% weight concentrations by weight.

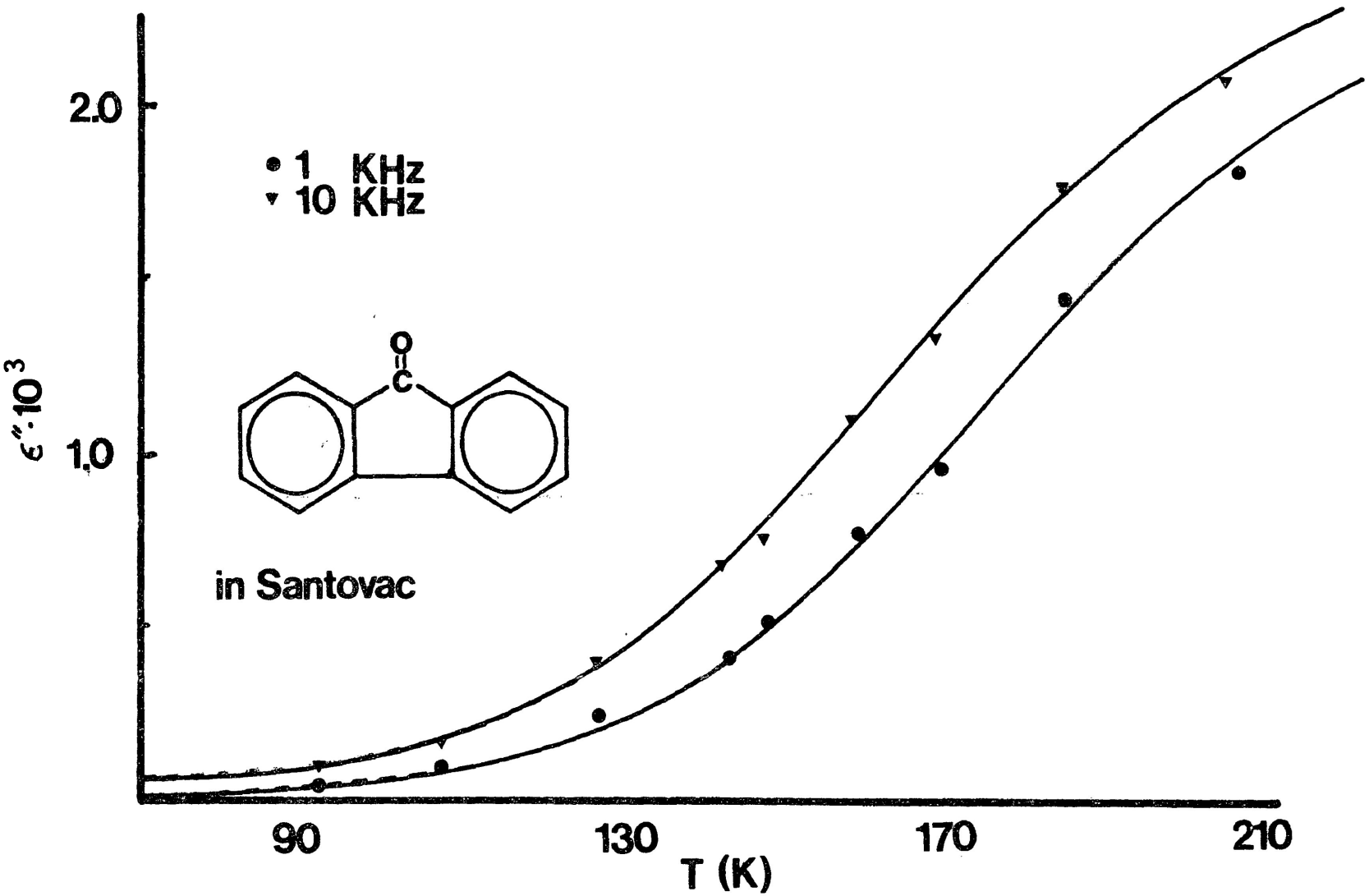


Figure VI-16 Dielectric loss plotted against temperature for a 5% by weight fluorenone solution.

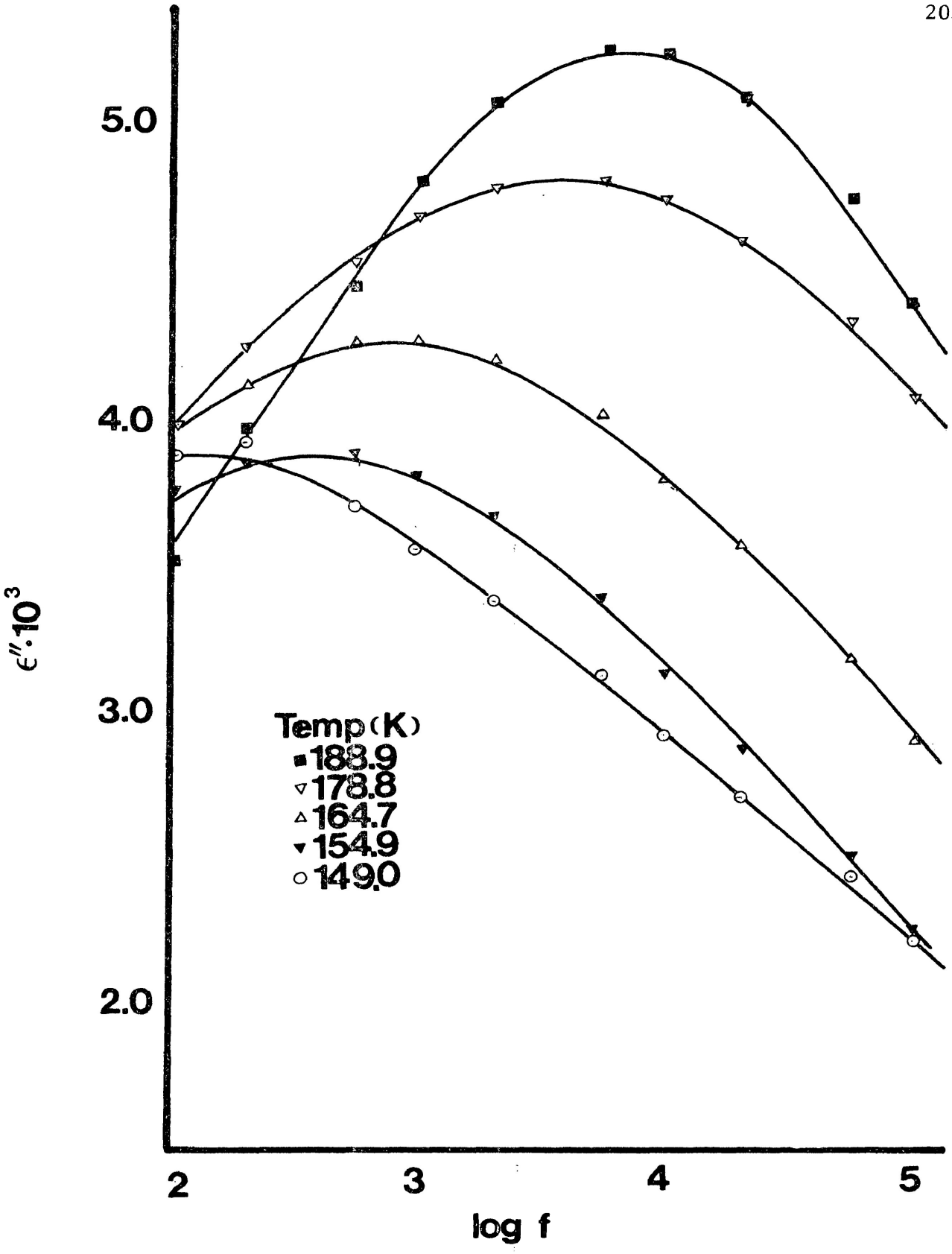


Figure VI-17 Dielectric loss versus log frequency for benzophenone (5% by weight in Santovac)

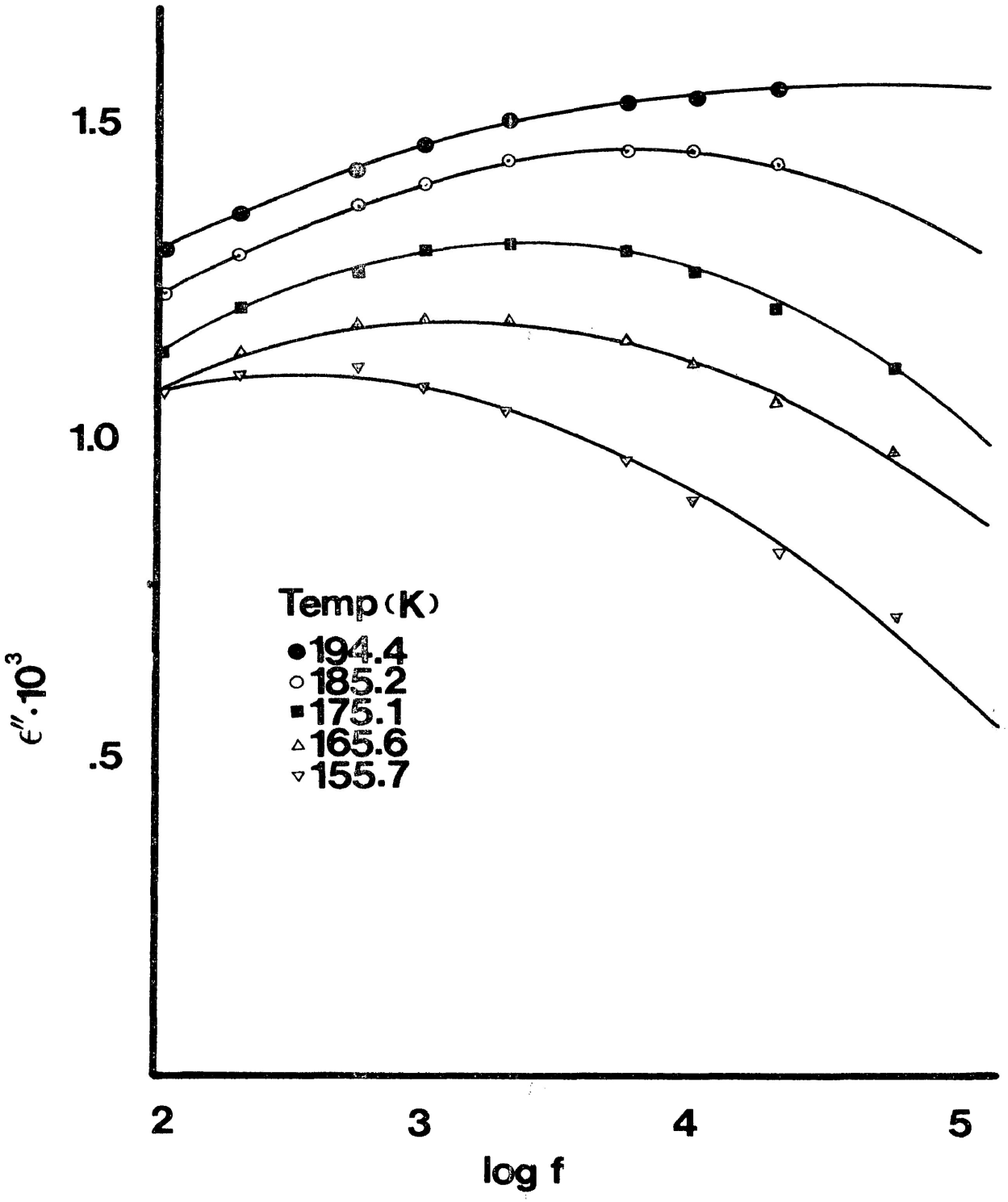


Figure VI-18 Dielectric loss versus log frequency for benzophenone (5% by weight in GOTP)

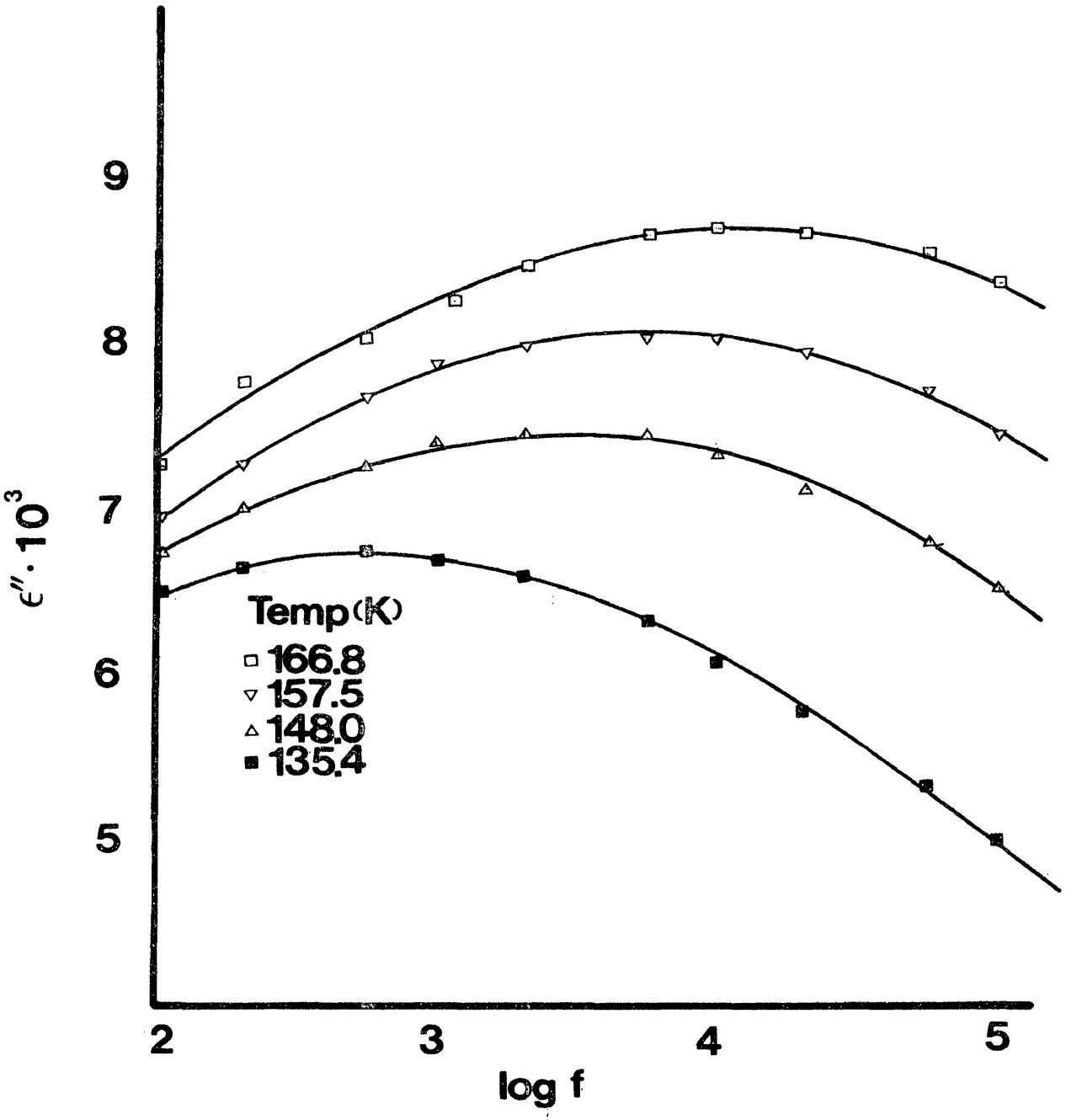


Figure VI-19 Dielectric loss versus log frequency for benzophenone (5% by weight in polystyrene)

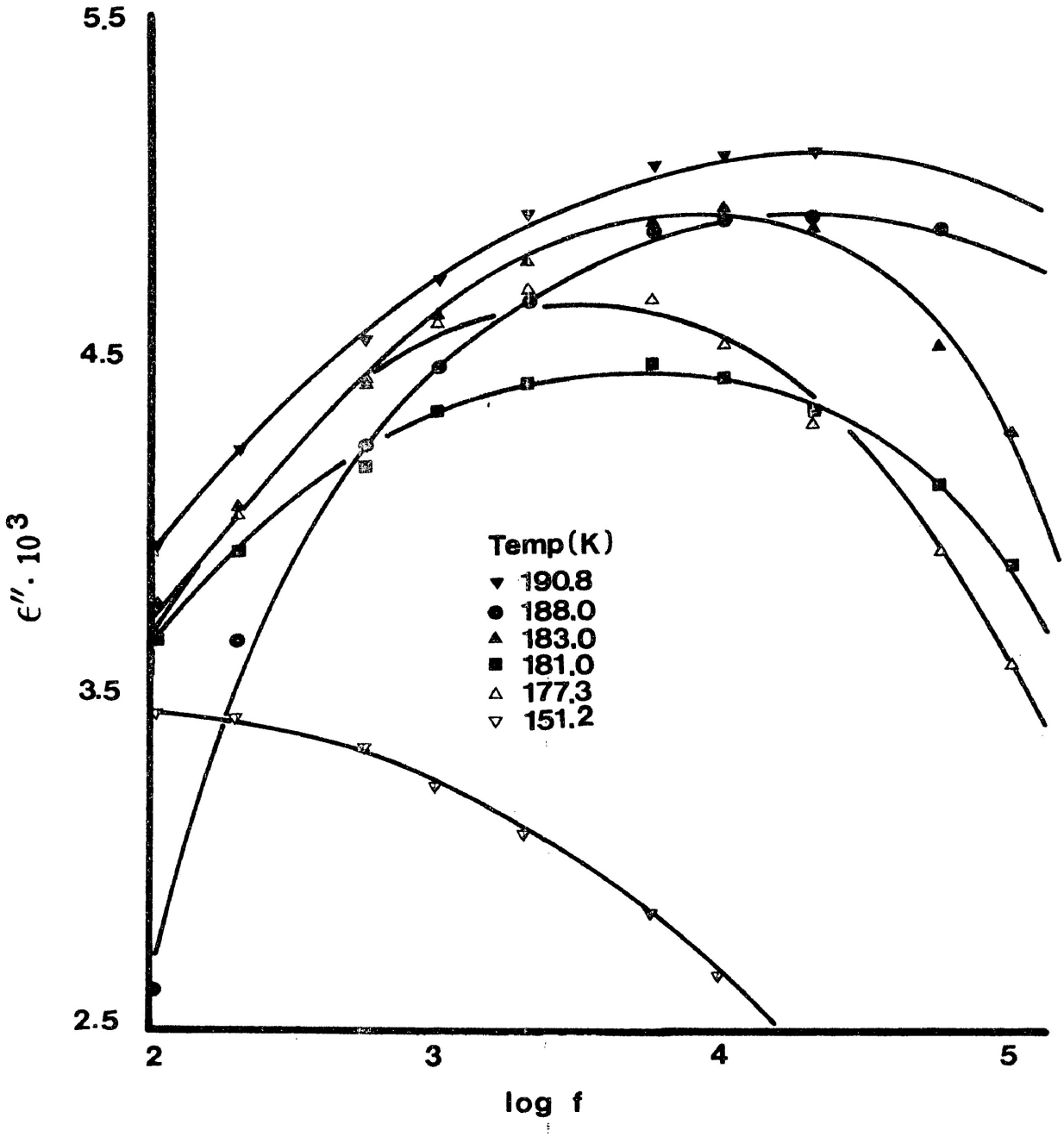


Figure VI-20 Dielectric loss versus log frequency for D_5-benzophenone (5% by weight in Santovac)

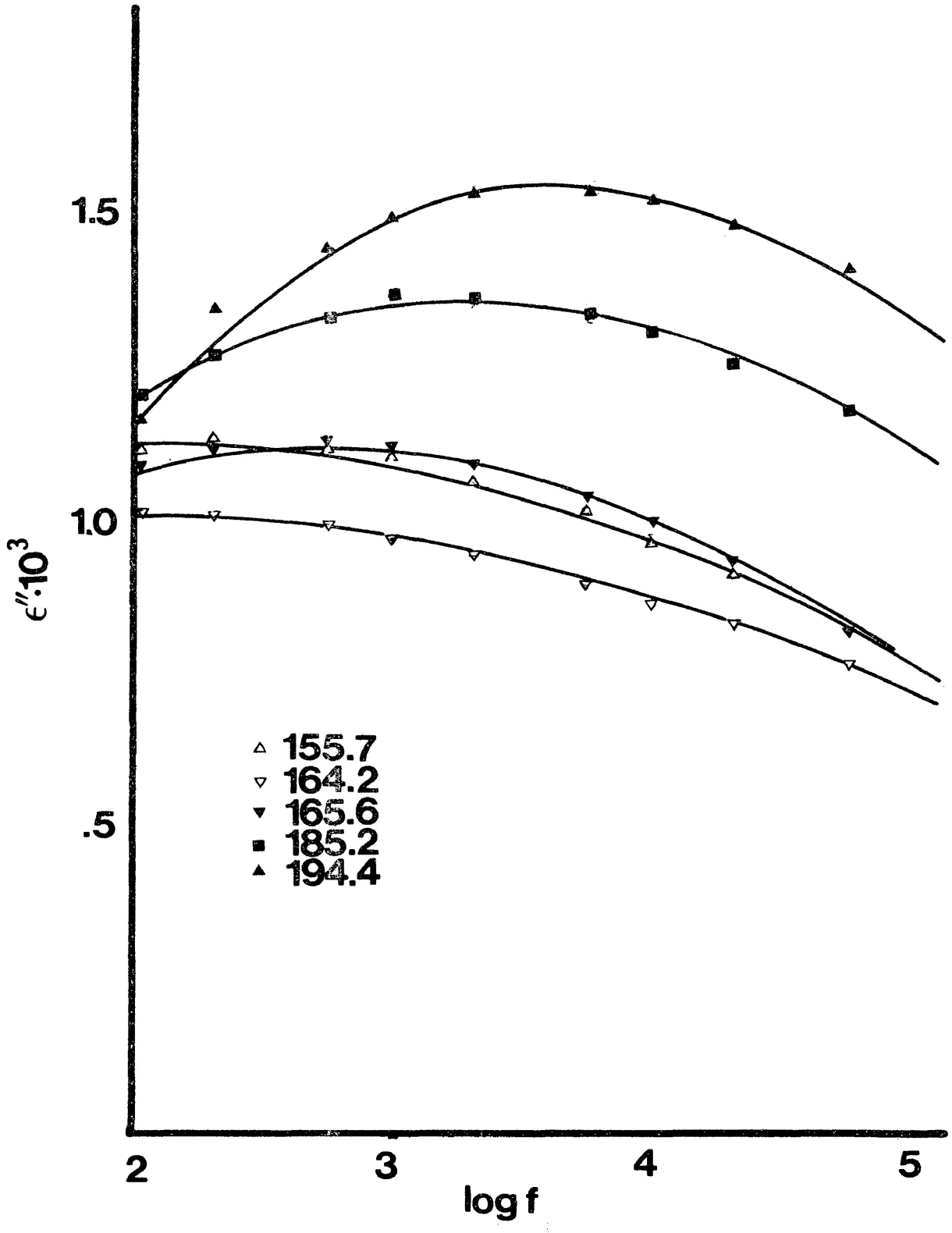


Figure VI-21 Dielectric loss versus log frequency for D_5-benzophenone (5% by weight in GOTP)

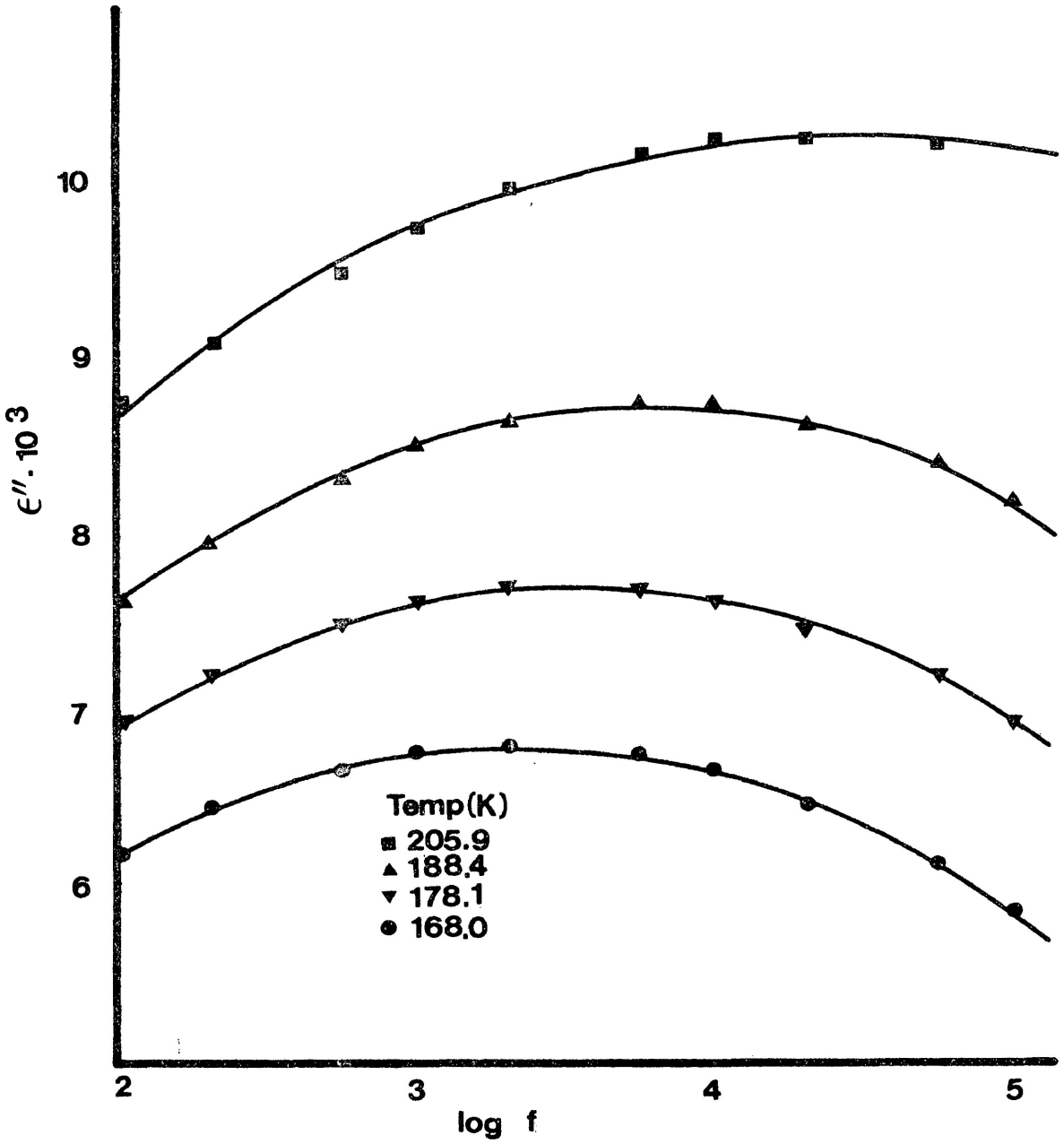


Figure VI-22 Dielectric loss versus log frequency for D_5-benzophenone (5% by weight in polystyrene)

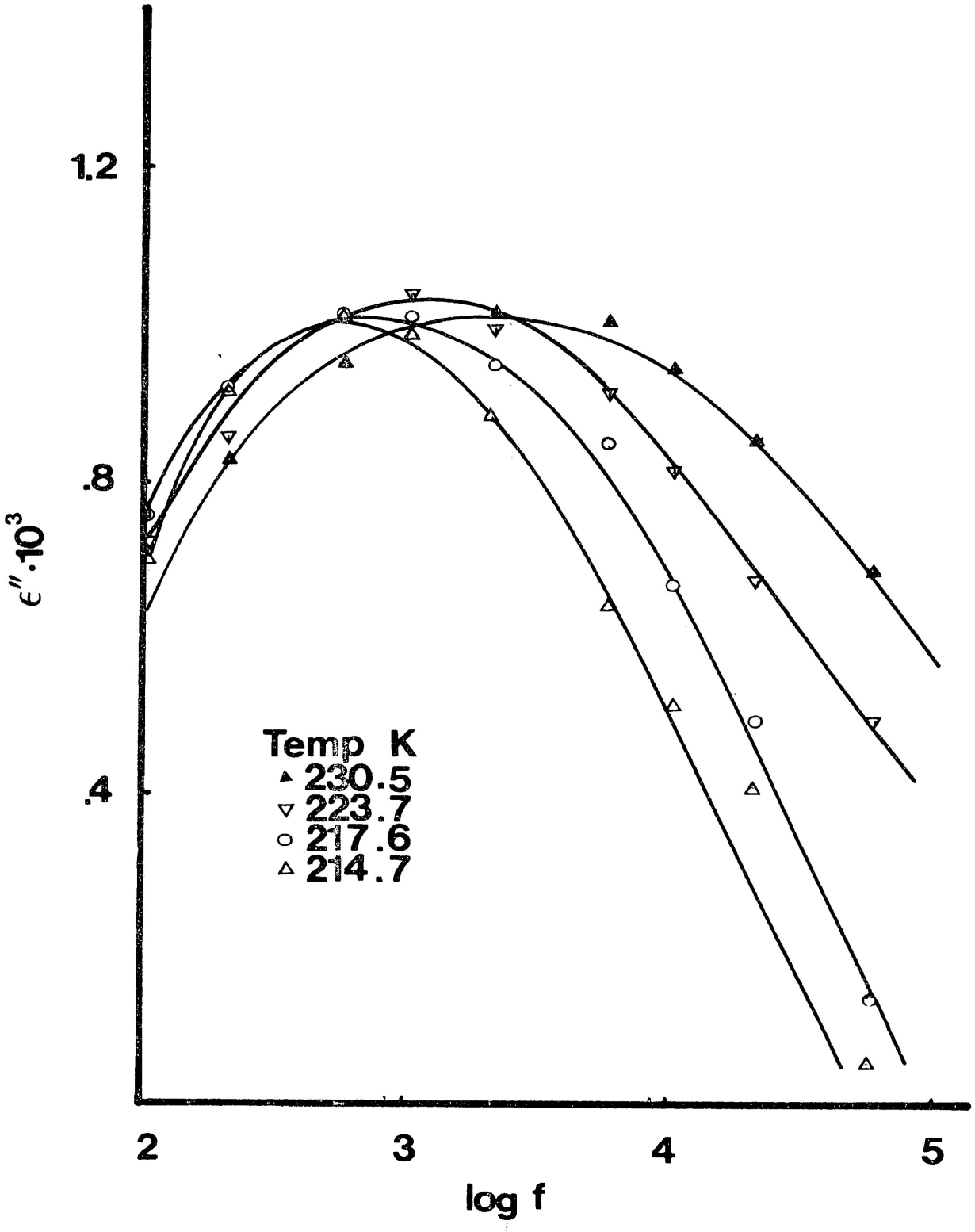


Figure VI-23 Dielectric loss versus log frequency for p-bromobenzophenone (5% by weight in GOTP)

ETHER BRIDGED MOLECULES

Maier [6], in liquid studies of diaryl ethers noted that the rigid molecule o-hydroxydiphenyl ether had a relaxation time at 293 K some 5 times greater than that observed for diphenyl ether itself. This, of course, is one of the studies which established the seemingly anomalous dielectric behavior of such molecules. Similar studies of the rigid molecule dibenzofuran show no such anomalous behavior.

Diphenyl ether has been studied by Desando [29] in polystyrene solutions and as the pure compressed solid at near liquid nitrogen temperatures and at frequencies as high as 10^8 Hz. He found in the compressed solid studies, extrapolated Eyring free energies of 6.8, 8.7 and 9.4 kJ mol^{-1} at 87.1, 105.0 and 112.1 K respectively. Although Desando was unable to observe experimentally loss maxima for this molecule, the low ΔG_E values indicate a very low energy process indeed. Similarly short relaxation times for this process were also calculated. At 87.1 K, the τ value has been estimated to be 6.6×10^{-9} s. Dielectric absorption maxima for diphenyl ether in

atactic polystyrene were observed in the frequency range of 10^2 to 10^5 Hz at temperatures of 213-235 K. Computer analysis of these loss curves gave ΔH_E as 74.7 kJ mol^{-1} and ΔS_E as 180.3 J K^{-1} mol^{-1}. The large entropy value may tend to suggest some sort of cooperative motion on the part of the solute with the polymer chains. The enthalpy value would not seem unreasonable for a molecule the size of diphenyl ether. The enthalpy value for dibenzothiophene as studied by Desando in polystyrene is 38.5 kJ mol^{-1}. This molecule, like its ketone counterpart fluorenone, is planar. A more realistic rigid molecule for comparison would be diphenyl sulfone. This molecule occupies considerably more volume since the phenyl rings, as in o-hydroxydiphenyl ether, maintain a more orthogonal orientation with respect to one another. The enthalpy of activation for this molecule is 62.0 kJ mol^{-1}. Thus, the value of $\sim$74 kJ mol^{-1} may represent a significant molecular component to the observed relaxation process.

In order to investigate the lower temperature process in diphenyl either more thoroughly, the disubstituted phenyl ether, bis(p-nitrophenyl) ether has been studied by this author as a solution in atactic polystyrene.

The para-nitro substitution pattern allows a quininoid structure to develop between the bridging oxygen atom and the nitro groups as below:

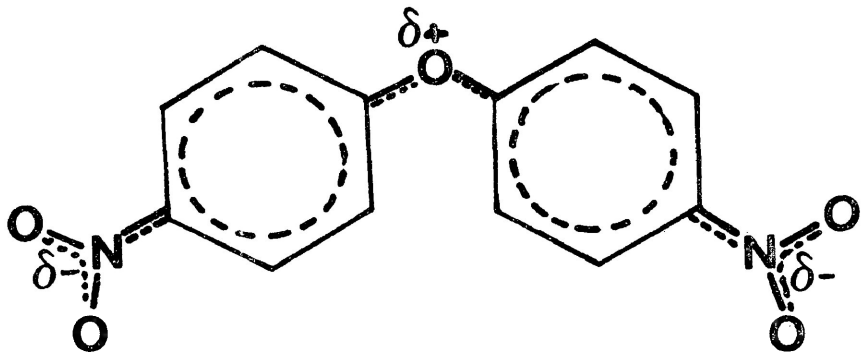


Figure VI-24 Electron distribution leading to increased double bond character in bis(p-nitrophenyl)ether

The increased electron density in the aryl-oxygen bond may increase its double bond character, and so one might expect an increase to the barrier of any relaxation process involving the bridging oxygen atom. From

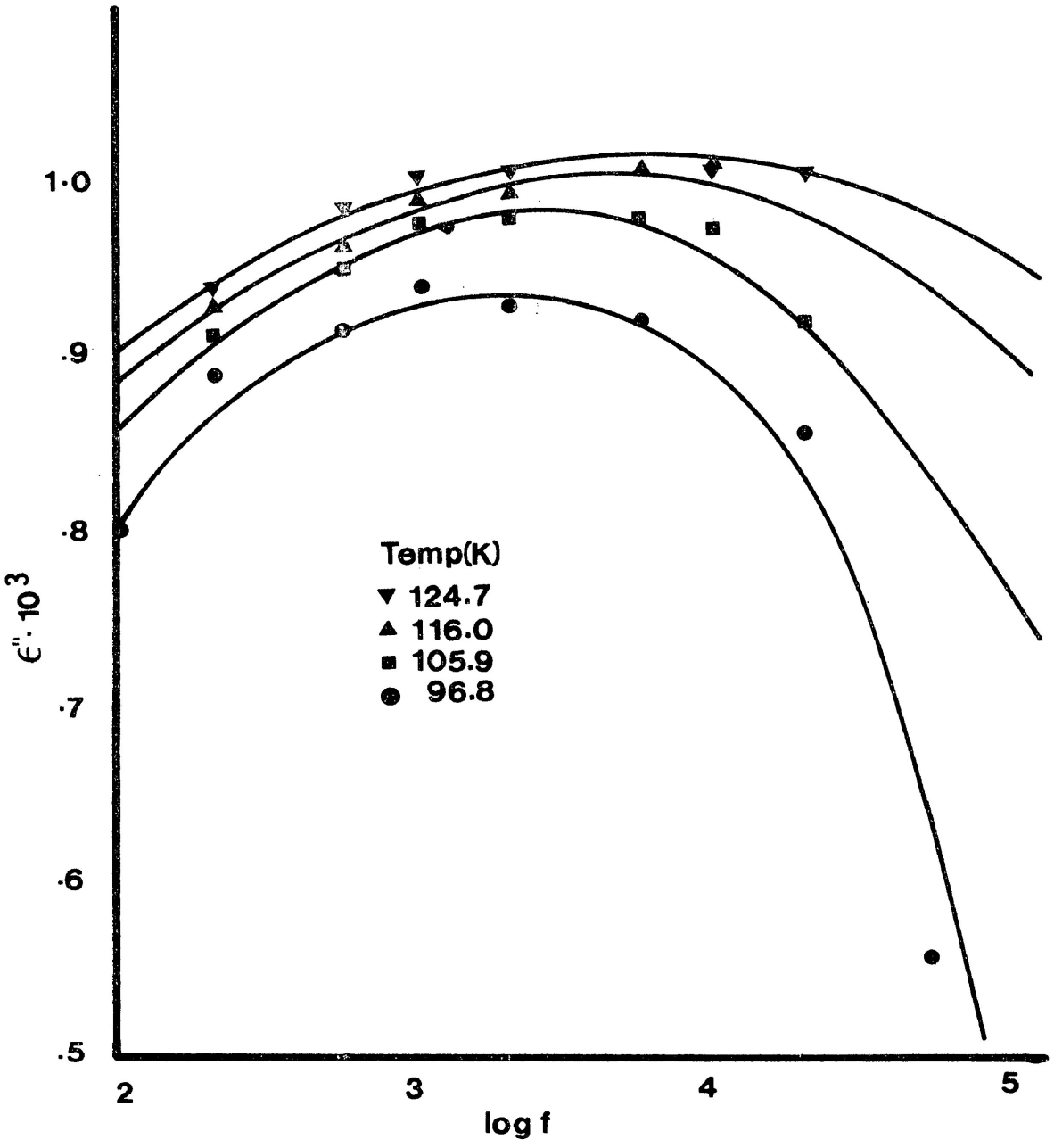


Figure VI-25 Dielectric loss curves of the group process observed with bis(p-nitrophenyl) ether (5% by weight in GOTP)

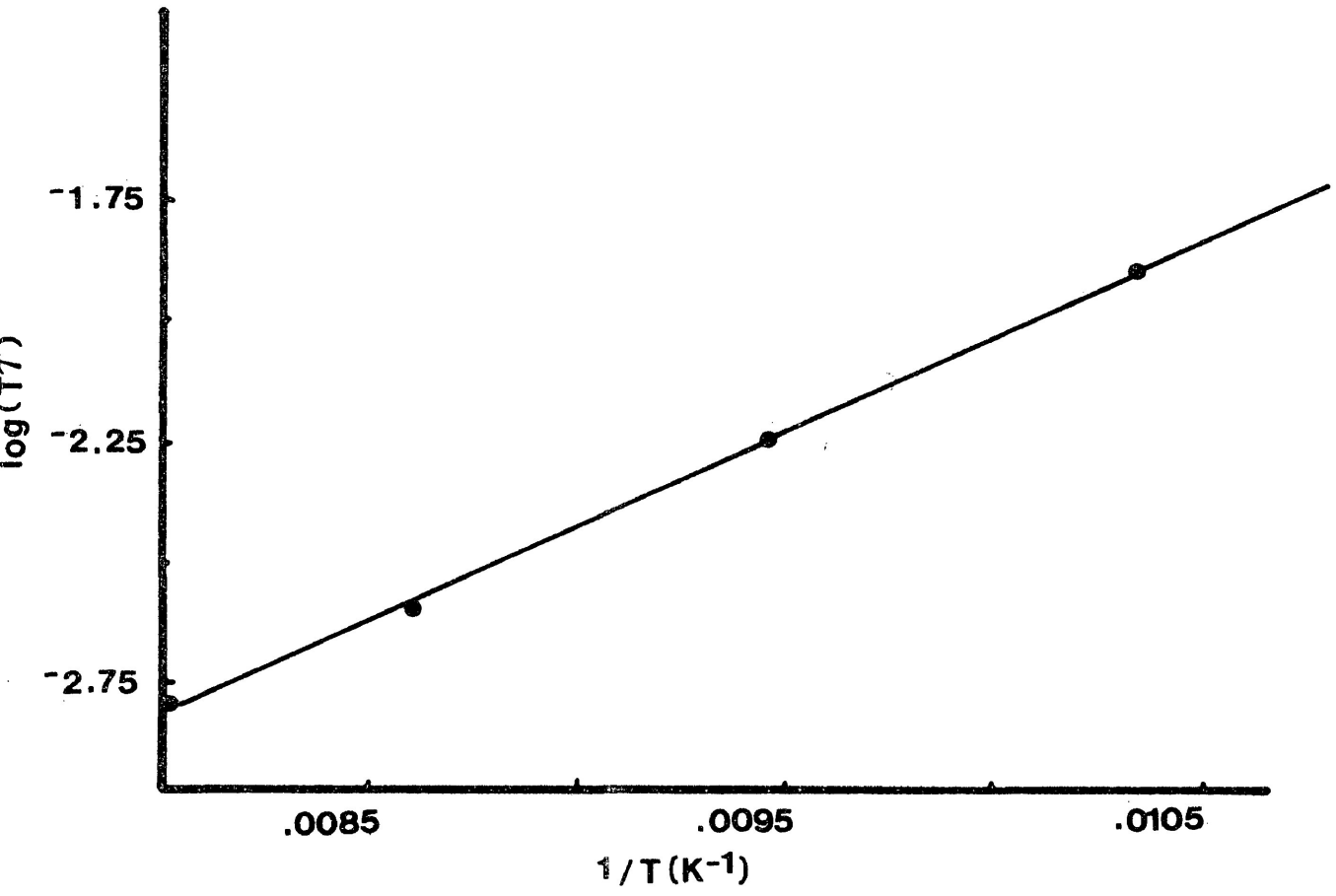


Figure VI-26 Eyring plot from previous loss curves.

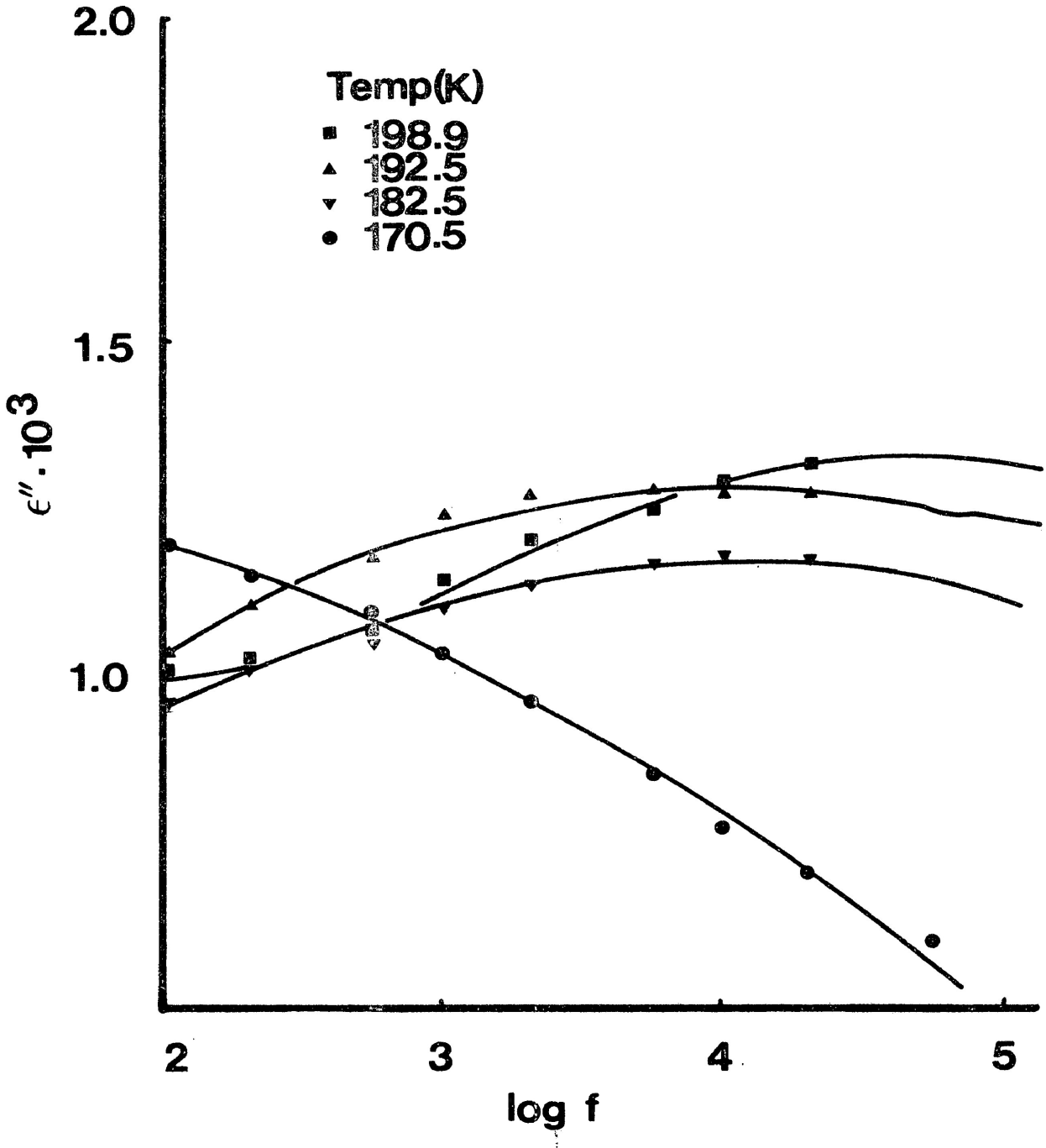


Figure VI-27 Loss curves for the molecular process of bis(p-nitrophenyl)ether (5% in GOTP).

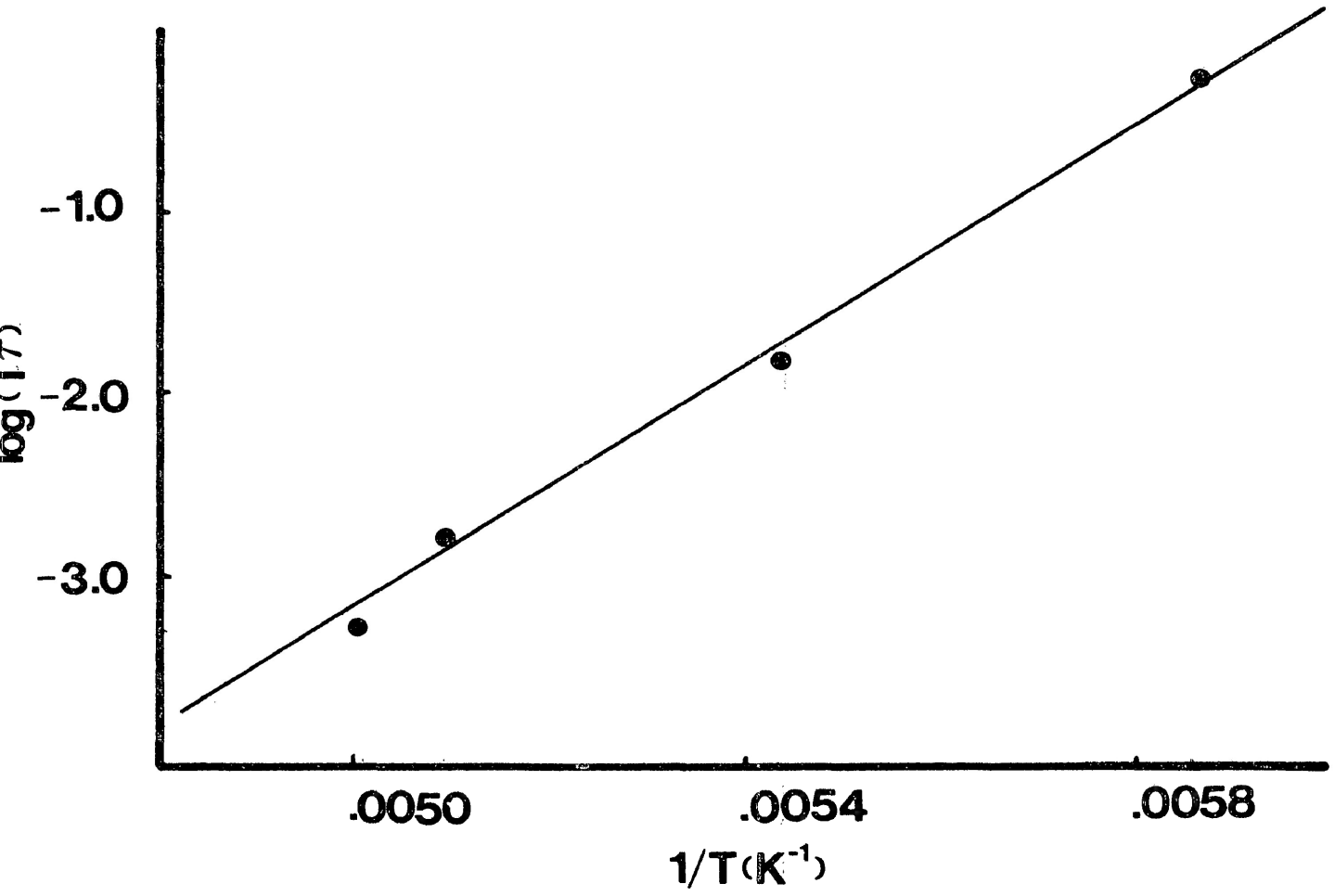


Figure VI-28 Eyring curve associated with the molecular process of bis(p-nitrophenyl)ether (5% in GOTP)

Table VI-3, the low temperature relaxation process observed for this molecule in polystyrene (weight-weight concentration of 8%) occurs over the temperature region 97-125 K the maxima of which have a $\log f_{max}$ range of 3.08-4.10. The enthalpy value as calculated from the $\log(T\tau)$ vs $1/T$ (K^{-1}) is rather low, $\sim$8 ±3 kJ mol^{-1}. The supposition, that increased electron density to the bridging group might increase the barrier to intramolecular motion, seems to be valid. A second, higher temperature process has also been observed over the range 171-199 K. The enthalpy of activation for this process is 71 ±9 kJ mol^{-1} with an entropy factor of 224 ±47 J K^{-1} mol^{-1}. The $\Delta G_{200\ K}$ has increased to 26.1 kJ mol^{-1} as compared to 24.1 for the low temperature process. Similarly, the $\tau_{200\ K}$ (s) values for the upper and lower temperature-processes are 1.58×10^{-6} s and 4.6×10^{-7} s respectively.

Another ether molecule studied in glassy o-terphenyl is interesting in the sense that there is a dipolar contribution along the principal axis from the para methyl group which virtually eliminates the molecular dipole component. The enthalpy value for this relaxation process is 7 ±3 kJ mol^{-1} while the entropy value is -68 ±14 J K^{-1} mol^{-1}. The average beta value, ($\bar{\beta}$), for this process

is 0.32. This is quite high for such a low temperature process and indicates a tendency toward a more discrete relaxation process. The short relaxation time of 7.3×10^{-7} s is in keeping with a very rapid, low energy methoxy group rotation. Most clearly, this molecule is relaxing by conventional group rotation.

One other point which should be stressed is that, in the case of bis(p-nitrophenyl)ether in polystyrene, this is the first example of a symmetric diaryl bridged molecule which has shown low and high temperature processes due to the molecularly dispersed solute in one sample.

SULFIDE BRIDGED MOLECULES

It was with the knowledge that these low energy processes are quite sensitive to the electron density in the bridging bonds, at least in terms of their Eyring parameters, that this author began to look at other bridged molecules which had shown a low temperature process but for which no molecular process had been recorded.

Diphenyl sulfide, a molecule of almost identical size to diphenyl ether, has a recorded ΔH_E value of 13.6 kJ mol^{-1} [29] in atactic polystyrene, as reported by Desando. Sulfur has a greater electron density than oxygen and so would likely show a greater electron density in the bridging bonds. The almost 6 kJ mol^{-1} increase in enthalpy of activation for this molecule over that of bis(p-nitrophenyl) ether supports the assertion (cf. Chapter 5) that Eyring parameters for intramolecular motions are indeed more sensitive to the nature of the bond(s) through which the molecule relaxes than to the media in which the process is studied.

Since the molecular process for bis(p-nitrophenyl) ether had been located, there seemed little reason that a similar high temperature process should not be detectable in the polystyrene/diphenyl ether sample. Again, reference to Table VI-2 details this very process. The temperature region, 207-231 K, over which this process was observed, revealed a process again with quite a large $\bar{\beta}$ value of 0.34, $\Delta G_{200\ K}$ = 35.5 kJ mol^{-1} and ΔH_E and ΔS_E values of 66 ±5 kJ mol^{-1} and 154 ±23 J K^{-1} mol^{-1}, respectively.

A slightly larger molecule, bis(p-tolyl)sulfide also studied by Desando [22] gave a ΔH_E value of 16.2 ±3 kJ mol^{-1} over the temperature region 93-106 K. The $\Delta G_{200\ K}$ is 5.6 kJ mol^{-1}. If this is compared to a more recent study of this system with the view to establishing a molecular barrier, the results are quite different: the ΔH_E and ΔS_E values are ∿69 kJ mol^{-1} and 191 J K^{-1} mol^{-1} respectively. Moreover, the $\Delta G_{200\ K}$ for this process is ∿31 kJ mol^{-1}.

It may now be stated with some degree of certainty that:

1) it is possible to observe both the low temperature, intramolecular process and the higher temperature molecular process within the same sample in at least some of these diaryl bridged molecules and

2) in at least the cases of benzophenone and its deuterated analogue, the most likely mechanism at work in the intramolecular process is that of a mesomeric shift of charge.

It should be pointed out that there is considerable variation in the magnitude of the loss observed

for molecules studied in various media. Inasmuch as loss is a function of concentration, and that solubility of the solute under study in a given medium plays a role in the ability of a solute/solvent system to achieve a given concentration, these solubility effects must be considered when comparing loss magnitudes. In general, temperature/logf_{max} ranges in conjunction with Eyring parameters seem to adequately identify a process under study, bearing in mind available data for appropriate sized rigid molecules.

While it is not possible to rule out any one particular mechanism in the remaining diaryl molecules with the data presented in this text, future studies along the lines discussed previously may assist in elaborating on this most interesting class of molecules.

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CHAPTER VII

CONCLUSIONS AND FUTURE WORK

CONCLUSIONS AND FUTURE WORK

To conclude this thesis, the two major aspects examined will be summarized. Clearly, one of the purposes of this research was to explore the constraints placed upon relaxing rigid molecules the dipole moments of which reside along the long molecular axes. To this end, the following empirical relationships were observed for the rigid molecules studied:

ΔH_{GOTP} vs $\Delta H_{P.S.}$	$\Delta H_{P.S.}=0.5\Delta H_{GOTP} + 3.3$	IV-1
ΔG_{GOTP} vs $\Delta H_{P.S.}$	$\Delta G_{P.S.}= 0.63\Delta G_{GOTP} + 4.6$	IV-2
$\bar{V}_{mean}$ in $\mathring{A}^3$ vs ΔG	$\Delta G_{GOTP}= 0.16\bar{V}_{swept} -17.6$	IV-3
$\bar{V}_{mean}$ in $\mathring{A}^3$ vs ΔH	$\Delta H_{GOTP}= 0.21\bar{V}_{swept} -36.8$	IV-4

In addition, for rigid molecules of this type, the limiting volumes swept out during the molecular relaxation process in glassy o-terphenyl seem to *ie.* between $\sim$216 $\mathring{A}^3$ and 340 $\mathring{A}^3$. This implies that for flexible molecules studied within this 'volume' range, absorption maxima (or overlap)

due to the molecular process can be expected within the temperature limits of the study, i.e. from near liquid nitrogen temperature up to the glass transition temperature for that particular solution in the frequency range for which these limits were determined, 10^2-10^5 Hz.

Further to this, it must now be recognized that particularly with low loss materials, tail end contributions of processes, the absorption maxima of which are well removed from the frequency/temperature range being studied, can play a significant role in determining the shape of the observed process and thereby affect the absolute Eyring parameters obtained.

The second aspect of this study involved flexible molecules, most of which are capable of both molecular and intramolecular relaxation processes. In order to determine the nature of the observed processes, comparisons were made with the behavior of relevant rigid molecules in the same media. In many cases, comparisons were made between results obtained in glassy o-terphenyl and media such as polystyrene and Santovac®. Generally, Eyring parameters determined were in agreement

within experimental errors with those determined by other workers using glassy o-terphenyl and other solvent systems. In certain cases, the pure samples were measured as compressed solids. For those molecules, which are not solids at room temperature, a new technique has been developed. The values obtained by this method seem to be lower than expected. Clearly the properties of compressed solids in terms of such factors as amorphic and polymorphic states as well as possible internal field effects, which might alter the intramolecular energy barrier, need to be explored further.

The flexible molecule theme of this work has been divided into two areas of study. The first of these, Chapter V, is an attempt to show, at least with carbonyl containing compounds, that the relaxation characteristics of these relatively media insensitive groups are, in fact, a result of the electron density (that is to say the degree of double bond character) of the bond about which the group relaxes and not so much the physical size of the relaxing entity. This, in the case of aromatic substituted ketones, most likely is a consequence of the thickness of the aromatic ring and the resultant space

in terms of displaced solvent molecules afforded the group for relaxation. In fact, the relaxing groups are often able to rotate almost within the thickness of the benzene ring itself.

The second aspect of this thesis, which is to examine special flexible molecules (Chapter VI), explores to a limited extent, the mechanistic path through which the 'bridged diaryl' molecules relax. Results for other molecules studied in polystyrene with bis(p-nitrophenyl) ether directly and, in the case of diphenyl ether, indirectly have proved that both the intramolecular and molecular processes can be observed in the same sample for these types of molecules.

The tail end of an intramolecular process has been found by Desando (cf. Chapter VI) with compressed solid work with diphenyl ether. The molecular process and, resultant Eyring parameters for this molecule have been observed in polystyrene and are in good agreement with Eyring parameters determined for a slightly larger ether, namely bis(p-nitrophenyl) ether.

The evidence leading to Desando's observation,

that the partial loss curves found at very low temperatures in the compressed solids are due to a low energy intramolecular process, is supported by this worker's detection of a low energy, low temperature process for diphenyl sulfide in polystyrene. On the assumption that the anomalous behavior of such molecules is a consequence of some concerted relaxation mechanism about the bridging atom, the increased electron density found in the C-S bonds of diphenyl sulfide would tend to raise the barrier to relaxation through the carbon-sulfur bridge. In fact, the Eyring parameters have been determined for diphenyl sulfide in polystyrene.

From the review presented in Chapter VI, benzophenone has been thought to relax predominantly by a molecular process as in the case of rigid molecules.

A genuine intramolecular process, probably broadened by the tail end of an overlapping molecular process, has now been detected in a number of solvent systems. In order to gain an insight into the mechanism by which this molecule relaxes, a deuterated analogue has been synthesized which was studied under similar conditions to its un-

deuterated counterpart, benzophenone.

In all three media, the deuterated molecule showed dielectric behavior virtually identical to that of the undeuterated benzophenone. The absorption maxima were found over the same temperature/frequency ranges, in both molecules, in each solvent system. Inasmuch as the deuterobenzophenone and benzophenone differ only in the position of the molecular centre of mass, the mechanism of double internal rotation should be considered untenable in both cases.

Of course, it does not necessarily follow that the anomalous dielectric behavior of other bridged diaryl molecules such as diphenyl ether, diphenyl sulfide, and their derivatives relax in the same fashion as benzophenone.

The technique of selective deuteration to alter the centre of mass of a molecule could be used in the study of a diphenyl sulfide series beginning with:

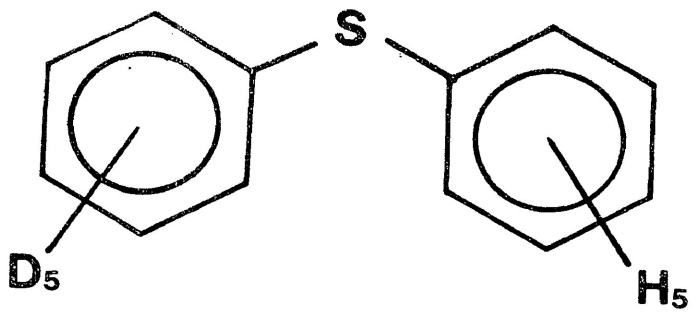

Figure VII-1 D_5-Diphenyl sulfide

Of course, the bridging atom could be varied too, for example, the sulfone. Symmetric or asymmetric substitution of these molecules, through the isotopic technique or otherwise, should also be explored.

Each of the molecules suggested for study in this section can all be synthesized using quite conventional organic techniques. As well, the precursors to these types of molecules are readily available from commercial supply houses.

LIST OF TABLES

LIST OF FIGURES

A P P E N D I X

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∇EYRING[⎕]∇
 EYRING;FACTOR;LOGIC;NAME;I;J;DUMMY;G;TAU;
TCALC;TINV;LTT;DH;DS;TABLE;MX;SX;MY;SY;SC1;
SC2;TEMP;FREQ
⍝THIS PROGRAM CALCULATES EYRING ΔH AND ΔS FR
OM FREQ(MAX) AND TEMP.
⍝IT REQUIRES THE FUNCTION DFT FROM LIB 1, WS
NAME PLOTFORMAT,∇
⍝PLUS THE VARIABLE ⍞KSP FOUND IN LIB 8, WSNA
ME CORRELATION.
 TITLE←NAME←⎕ ,0⍴⎕ ←' TITLE '
 'ENTER TEMP. AND FREQ. DATA EITHER AS VECTO
RS OR AS SEPARATE PAIRS? '
 'ENTER VECTORS?  YES OR NO.'
 →('Y'∈DUMMY←⎕)/15
 (⍕'TYPE IN PAIRS'),(⍕(5⍴⍞KSP)),(⍕(5⍴'_')),(
⍕' OF NUMBERS, TEMP (∘C)'),(⍕(3⍴⍞KSP)),(⍕'__
'),⍕'  FIRST, THEN FREQ(MAX) OR LOG OF FREQ(
MAX).'
 'WHEN FINISHED, TYPE \0 ON A NEW LINE.'
 FREQ←TEMP←⍳0
 →((0 2)=⍴I←⎕ )/ 21 13
 →11,0⍴(⎕ ←'RE-ENTER LAST LINE AS A PAIR',(4
⍴⍞KSP),'____ OF NUMBERS.')
 TC←TEMP←TEMP,I[1]
 →11,⍴FREQ←FREQ,I[2]
 (⍕'ENTER THE VECTOR (OR ITS NAME) OF TEMPS
IN ∘C.'),(⍕3⍴⍞KSP),⍕'__'
 TC←TEMP←⎕
 'ENTER THE VECTOR (OR ITS NAME) OF FREQUENC
IES (IN HERTZ) OR LOG(FREQ).'
 FREQ←⎕
 →((⍴FREQ)=⍴TEMP)/2+⍳26
 →15,0⍴⎕ ←'UNEQUAL NUMBERS OF ITEMS ENTERED
ABOVE.'
 (⍕'YOU HAVE ENTERED TEMPS (∘C) AS:'),⍕TEMP
 (⍕'AND FREQ AS:'),⍕FREQ
 'ARE THESE ALL CORRECT? (YES OR NO)'
 →('N'∈DUMMY←⎕)/CORR
 →(2<I←⍴FREQ)/27
 →0,⍴⎕ ←'YOU ENTERED LESS THAN THREE PAIRS O
F DATA, I QUIT.'
 →(I=+/(20>FREQ))/30
 FREQ←10⍟FREQ
 'I HAVE CONVERTED FREQUENCIES TO LOGS.'
 TINV←÷TEMP←273+TEMP
 LTT←(10⍟TEMP÷⍟2)-LF←FREQ
⍝CALCULATE REGRESSION LINE OF LTT VS TINV, A
ND ASSOCIATED CONFIDENCE INTERVALS.
 SX←TINV-(MX←+/TINV÷I)
 SY←LTT-(MY←+/LTT÷I)
 COEFF←(+/SX×SY)÷+/SX*2
 COEFF←COEFF,(MY-MX×COEFF)
 J←1+0×⍴CALC←⍳0
 CALC←CALC,(TINV[J]⊥COEFF)
 →(I≥J←J+1)/⍳1+⍳26
 SX←+/SX*2
 SY←(+/(LTT-CALC)*2)÷I-2
 SC1←(SY÷SX)*0.5
 SC2←(SY×(÷I)+(MX*2)÷SX)*0.5
⍝NOW PICK OUT THE APPROPRIATE LINE OF A STUD
ENT T-TABLE FOR (I-2) DEGREES OF FREEDOM.
 →(16>TABLE←⍳2+I)/2+⍳26
```

```
 TABLE←15
 →TABLE+⍳26
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63.657
 →14+(⍳26),⍴TABLE← 2.92 4.303 6.965 9.925
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 →12+(⍳26),⍴TABLE← 2.132 2.776 3.747 4.604
 →11+(⍳26),⍴TABLE← 2.015 2.571 3.365 4.032
 →10+(⍳26),⍴TABLE← 1.943 2.447 3.143 3.707
 →9+(⍳26),⍴TABLE← 1.895 2.365 2.998 3.499
 →8+(⍳26),⍴TABLE← 1.86 2.306 2.896 3.355
 →7+(⍳26),⍴TABLE← 1.833 2.262 2.821 3.25
 →6+(⍳26),⍴TABLE← 1.812 2.228 2.764 3.169
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 TABLE← 1.753 2.131 2.602 2.947
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 DS←(¯1.987 ¯8.3143)×FACTOR×(COEFF[2]+10.319
)
⍝NOW TO CALCULATE ΔG AND TAU AT SEVERAL TEMP
ERATURES.
 G←DH[2]-DS[2]×(TCALC←100,150,200,225,293,
298,300)÷1000
⍝CHECK FOR VALUES OF G TOO LARGE, ALTER IF N
ECESSARY.
 →(0=+/LOGIC←(174≤G×1000÷TCALC×8.3143)/⍳⍴G)/
2+⍳26
 G[LOGIC]←1
 TAU←(4.7993E¯11÷TCALC)**G×1000÷TCALC×8.3143
 →(0=+/LOGIC)/5+⍳26
 G[LOGIC]←DH[2]-DS[2]×TCALC[LOGIC]÷1000
 J←1
 TAU[(LOGIC[J])]←0-((÷TCALC[(LOGIC[J])])⊥
COEFF)-10⍟TCALC[(LOGIC[J])]
 →((⍴LOGIC)≥J←J+1)/¯1+⍳26
 DUMMY←⍞,0⍴⍞ ←'ROLL PAPER UP TO NEW SHEET, P
RESS ''RETURN''.'
 ⍝')OUTPUT DSK:ÅPLSF.APL'
 NAME
 (⍴NAME)⍴'¯'
 (↑'INPUT AND CALCULATED DATA'),(↑25⍴⎕BKSP),↑
25⍴'_'
 '     TEMP       1000÷T     LOG F      F(KHZ)
 LOG TTAU  LOG TTAU'
 '      (°K)       (°K)*¯1    (OBS)      (OBS)
  (OBS)      (CALC)'
 J←1
 10 3 ⎕FT(TEMP[J],(1000×TINV[J]),FREQ[J],(10
*FREQ[J]-3),LTT[J],CALC[J])
 →(I≥J←J+1)/¯1+⍳26
 (↑'RMS DEVIATION FOR LOG TTAU = +/- '),↑(+/
((CALC-LTT)*2)÷I)*0.5
 ⍞ ←' '
 (↑'GRAPH SLOPE IS: '),(↑COEFF[1]),↑' °K'
 (↑'EYRING ΔH = '),(↑DH[1]),(↑' KCAL./MOLE,
OR      '),(↑DH[2]),↑' KJOULES/MOLE.'
 (↑'GRAPH INTERCEPT IS: '),↑COEFF[2]
 (↑'EYRING ΔS = '),(↑DS[1]),(↑' CAL./DEG.-MO
LE, OR '),(↑DS[2]),↑' JOULES/DEG.-MOLE.'
 '    CALCULATED VALUES OF ΔG AND TAU:'
⍝PRINT WARNING IF VALUES OF ΔG WERE TOO LARG
```

```
   E.
]  (  →(0=+/LOGIC)/4+⍳26
]     '      WARNING: VALUES OF TAU COULD NOT BE C
   ALCULATED AT SOME TEMPERATURES.'
]     (⍕'                THIS OCCURRED FOR TEMPS. (
   °K) OF: '),⍕TCALC[LOGIC]
]     (⍕'                FOR THESE CASES, THE ENTRI
   ES IN THE TABLE ARE THE NEGATIVE'),(⍕8⍴⎕KSF)
   ,(⍕8⍴'_'),⍕' LOG OF TAU.'
]     '      TEMP          ΔG           TAU          F.
   MAX.'
)]    '       (°K)       (KJ/MOLE)      (SEC.)       (C
   /S)'
1]    ⎕←(4 7 ⍴(TCALC,G,TAU,÷⎕←2×TAU))
2]    '      ERROR ESTIMATES:'
3]    21⍴'-'
4]    (⍕'       THERE ARE '),(⍕¯2+I),⍕' DEGREES OF
   FREEDOM.'
5]    →(I<18)/2+⍳26
6]    '      WARNING: CONFIDENCE INTERVALS HAVE BE
   EN CALCULATED FOR ONLY 15 DEGREES OF FREEDOM
   !'
7]    '                                          CONFIDE
   NCE INTERVAL WIDTHS'
8]    '      QUANTITY                    90°/°      95
   °/°      98°/°      99°/°'
9]    '      ΔH (KCAL/MOLE)   +/- ',(10 4 DFT 1.987
   ×TABLE×FACTOR×SC1÷1000)
0]    '           (KJ/MOLE)   +/- ',(10 4 DFT
   8.3143×TABLE×FACTOR×SC1÷1000)
1]    '      ΔS (CAL/°-MOLE) +/- ',(10 4 DFT 1.987
   ×TABLE×FACTOR×SC2)
2]    '           (J/°-MOLE)  +/- ',(10 4 DFT
   8.3143×TABLE×FACTOR×SC2)
3]    ⎕←')OUTPUT'
4]    'COLLECT OUTPUT AT NEAREST LINE PRINTER'
5]    →0
6]    'ROLL UP TO NEW SHEET AND PRESS ''RETURN''
   FOR ERRORS ON LOG(TxTAU).'
7]  . DUMMY←⍞
8]    NAME
9]    (⍴NAME)⍴'-'
0]    ' '
1]    (⍕'       THERE ARE '),(⍕¯2+I),⍕' DEGREES OF
   FREEDOM.'
2]    →(18>I)/2+⍳26
3]    '      WARNING: CONFIDENCE INTERVALS HAVE BE
   EN CALCULATED FOR ONLY 15 DEGREES OF FREEDOM
   !'
4]    SC1←SC1←SY×(÷I)+((TINV-MX)*2)÷SX
5]    SC2←SC1←SY
6]    ' '
7]    (⍕'      CONFIDENCE INTERVALS FOR CALCULATED
   '),(⍕10⍴⎕KSF),(⍕10⍴'_'),⍕' VALUES OF LOG(TxT
   AU)'
8]    '      TEMP      1000÷T   LOG(TxTAU)          CO
   NFIDENCE INTERVAL WIDTHS'
9]    '       (°K)      (°K)*¯1    (CALC)      90°/°
      95°/°      98°/°      99°/°'
0]    J←1
1]    10 3 ⎕DFT(TEMP[J],(1000×TINV[J]),CALC[J],(
   TABLE×SC1[J]))
2]    →(I≥J←J+1)/¯1+⍳26
3]    ' '
```

```
∇FUOSSK[□]∇
∇  FUOSSK;MX;SX;MT;ST;TABLE;LOGIC;LOG;HYP;FF;
BLFF;DI;B0;B1;FM0;I;I1;J;S;SB1;TV;X0;PS;FC
  'TYPE ''N'' IF YOU DO NOT ENTER NEW DATA, E
LSE TYPE ''Y'''
  →('N'ε□)/L11
  TITLE←□ ,0ρ□ ←'TITLE'
  TEMP←□ ,0ρ□ ←'TEMPERATURE IN DEG C◦ OR K◦'
  →(TEMP>75)/2+⍳26
  TEMP←273+TEMP
  TC←¯273+TEMP
  F←□ ,0ρ□ ←'ε''''  ; FROM LOW FQ'
  FQ←□ ,0ρ□ ←'FREQ IN   C/S ; FROM  LOW TO HI
GH '
  'TO NEW PAGE, PRESS RETURN'
  □
  (⍎SP 1),⍎TITLE
  (ρTITLE)ρ'¯'
  (⍎('
T TEMPERATURE = 273 + ')),(⍎(¯273+TEMP)),(⍎' =
  '),(⍎TEMP),⍎' ◦K'
  ((⍎'  FREQ(C/S)    ε''''  OBS'),⍎SP 2)
  □(2,ρF)ρFQ,F
  →(4+⍳26)
L11:TITLE
  (ρTITLE)ρ'¯'
  (⍎('
T TEMPERATURE = 273 + ')),(⍎(¯273+TEMP)),(⍎' =
  '),⍎TEMP
  ((⍎'  ε''''OBS  '),⍎SP 1)
  25 100 PLOT F VS 10@FQ
  (⍎40ρ' '),⍎'LOG(FREQ)'
  'ARE THESE ε'''' CORRECT? YES OR NO'
  →('Y'ε□)/3+⍳26
  F←□ ,0ρ□ ←'ε''''  ; FROM LOW FQ'
  FQ←□ ,0ρ□ ←'FREQ IN C/S ; FROM LOW FQ'
  (⍎'TO NEW PAGE PRESS RETURN'),⍎SP 1
  □
  (⍎X0←X←1÷⍟2XX←□ ,0ρ□ ←'FREQ(MAX)(C/S) GUESS
'),⍎SP 3
  DI←□ ,0ρ□ ←'ε◎ OR ε'' AT THE LOWEST FREQUEN
CY'
  ('
F; POLYSTYRENE ε''')
  '¯193 2.62 ¯155 2.6 ¯120 2.57 ¯110 2.57 ¯10
0 2.58 ¯90 2.54 ¯80 2.55 ¯50 2.53 ¯20 2.54 0
2.53 20 2.51 60 2.5 70 2.5'
  DI←DI-FF←□ ,0ρ□ ←'εINF OR ε''SOLVENT'
  FM0←FM←0.8×DI÷2
  →((+/F≤FM0)=ρF)/2+⍳26
  FM0←0.0002+⌈/F
  (⍎'UPPER LIMIT OF ε''''MAX    =    '),(⍎FM0),
⍎SP 2
  (⍎'ANALYSIS IN PROGRESS, PLEASE LEAVE IT AL
ONE'),⍎SP 5
  SP 5
  J←ρFM←(100⌊J0←(⌈((FM0-⌈/F)÷1.0000E¯5 )+1))ρ
FM
  I←1
  FM[1]←1.0000E¯6 +⌈/F
  X[1]←1↑X←(J)ρX,0ρR←(J)ρ1,0ρSB1←(J)ρ1,0ρTV←(
J)ρ1,0ρB1←(J)ρ1,0ρB0←(J)ρ1,0ρRE←(J)ρ1
  HYP←¯6⊕(FM[1]÷F)
```

```
∇HYP[LOGIC]←Q-HYP[LOGIC←(FQ)÷○2×X[1])/⍳⍴FQ]
 (LOG←⍟(÷○2×FQ×X[1]))SR2 HYP
 X[1]←(÷○2××((⍟÷○2×X[1])+B0[1]÷B1[1]))
L13:I1←I
 HYP←¯6○(FM[I]÷F)
 HYP[LOGIC]←Q-HYP[LOGIC←(FQ)÷○2×X[I])/⍳⍴FQ]
 (LOG←⍟(÷○2×X[I]×FQ))SR2 HYP
 X[I]←(÷○2××((⍟÷○2×X[I])+B0[I]÷BE[I]←B1[I]))
 →((|R[I])=1)/L12
 →(FM[I]>FM0)/L12
 →(((|TV[I])<⌈/|TV)∧(I>20))/L12
 →(I1=100)/L12
 →(I1=J0)/L12
 I←I1+1
 FM[I]←FM[I1]+1.0000E¯5
 X[I]←X[I1]
 →L13
L12:TV←(I)↑TV
 'END, TO NEW PAGE, PRESS RETURN'
 SF 5
 □
 ε')OUTPUT DSK:APLSF.APL'
 TITLE
 (⍴TITLE)⍴'¯'
 (⍪'AT TEMPERATURE = 273 + '),(⍪(¯273+TEMP))
,(⍪' = '),(⍪TEMP),⍪' °K'
 ((⍪'WITH FIRST GUESS FOR ωMAX       = '),(⍪(
1÷X0)÷○2),(⍪'C/S'),⍪SF 1)
 ((⍪'NO OF TRIALS                    = '),⍪I)
 (⍪('BEST RESULTS FOUND AT TRIAL NO:  '),⍪I←
(|TV)⍳⌈/|TV)
 ((⍪'THE ε''''MAX                      = '),(
⍪FM←FM[I]),⍪SF 1)
 ((⍪'THE TAO(SEC) VALUE              = '),⍪X←
X[I])
 (⍪'THE ΔG(KJOULE/MOLE) VALUE      = '),⍪DG←
(÷1000)×8.3143×TEMP×(⍟X×TEMP)-⍟4.7993E¯11
 ((⍪'THE FQ-MAX(C/S)                 = '),⍪÷○
2×X)
 (⍪('(BASE 10) LOG OF FQ-MAX(C/S)    = '),⍪10
⍟(÷○2×X))
 ((⍪'THE BETA VALUE                  = '),⍪BE
←BE[I])
 ((⍪'THE CORRELATION COEFF FOR COSH¯1(ε''''M
/ε''''') VS LOG(FQ):  '),(⍪R[I]),⍪SF 1)
 ((⍪'THE STANDARD ERROR FOR THE SLOPE (BETA
VALUE) :          '),⍪SB1[I])
 ((⍪'THE T-VALUE FOR THE CORRELATION COEFFIC
IENT :            '),⍪TV[I])
 HYP←¯6○(FM÷F)
 HYP[LOGIC]←Q-HYP[LOGIC←(FQ)÷○2×X)/⍳⍴FQ]
 BLFF←BE×⍟(÷○2×X)÷FQ
 FC←FM÷¯6○(BLFF)
 (⍪'   FREQ(C/S)    ε''''OBS       ε''''CALC
 E2OBS/E2MAX E2CALC/E2MAX'),⍪SF 1
 ⍉(5,⍴FQ)⍴FQ,F,FC,(F÷FM),(FC÷FM)
ANOW TO ESTIMATE ERRORS.
 ' '
 '      ERROR ESTIMATES:'
 TABLE←¯2+⍴HYP
 (⍪'      RMS ERROR FOR ε''''     IS '),⍪(+/((
FC-F)*2)÷⍴F)*0.5
 (⍪'      RMS ERROR FOR COSH¯1 IS '),⍪(+/((
HYP-BLFF)*2)÷⍴F)*0.5
```

```
]    (⍕'      THERE ARE '),(⍕TABLE),⍕' DEGREES OF
     FREEDOM.'
]    →(16>TABLE)/2+⍳26
]    TABLE←15+0×⍴□ ←'      WARNING: CONFIDENCE IN
    TERVALS CALCULATED FOR ONLY 15 DEGREES OF FR
    EEDOM!'
]    →TABLE+⍳26
]    →15+(⍳26),⍴TABLE← 6.314 12.706 31.821
    63.657
0]   →14+(⍳26),⍴TABLE← 2.92 4.303 6.965 9.925
1]   →13+(⍳26),⍴TABLE← 2.353 3.182 4.541 5.841
2]   →12+(⍳26),⍴TABLE← 2.132 2.776 3.747 4.604
3]   →11+(⍳26),⍴TABLE← 2.015 2.571 3.365 4.032
4]   →10+(⍳26),⍴TABLE← 1.943 2.447 3.143 3.707
5]   →9+(⍳26),⍴TABLE← 1.895 2.365 2.998 3.499
6]   →8+(⍳26),⍴TABLE← 1.86 2.306 2.896 3.355
7]   →7+(⍳26),⍴TABLE← 1.833 2.262 2.821 3.25
8]   →6+(⍳26),⍴TABLE← 1.812 2.228 2.764 3.169
9]   →5+(⍳26),⍴TABLE← 1.796 2.201 2.718 3.106
0]   →4+(⍳26),⍴TABLE← 1.782 2.179 2.681 3.055
1]   →3+(⍳26),⍴TABLE← 1.771 2.16 2.65 3.012
2]   →2+(⍳26),⍴TABLE← 1.761 2.145 2.624 2.977
3]   TABLE← 1.753 2.131 2.602 2.947
4]   SX←+/(LOG-MX←+/(LOG←⍟(÷⍳2×⍴FQ))÷⍴FQ)*2
5]   ST←+/((HYP-BLFF)*2)÷¯2+⍴HYP
6]   '                                CONFIDENCE INT
    ERVAL WIDTH'
7]   '      QUANTITY              90%       95%
       98%       99%'
8]   (⍕'      BETA          +/-   '),⍕TABLE×(ST÷SX)
    *0.5
9]   ST←(B0[I]÷BE×⍟10)×(((STX(÷⍴LOG)+(MX*2)÷SX)*
    0.5)÷B0[I])+((ST÷SX)*0.5)÷BE
0]   (⍕'      LOG(FQ-MAX)   +/-   '),(⍕DLF90←STX
    TABLE[1]),(⍕'     '),(⍕STXTABLE[2]),(⍕'     '),
    (⍕STXTABLE[3]),(⍕'     '),⍕STXTABLE[4]
1]   ('
*********END OF PROGRAM*********')
2]   25 100 PLOT F VS 10⍟FQ
3]   ⍞')OUTPUT'
4]   'COLLECT OUTPUT AT NEAREST LPT'
5]   →(I<100)/0
6]   →((I>100)∧(I<J0))/0
7]   →(I=100)/3+⍳26
8]   ('THE RESULTS ARE FOR THE ASSUMED UPPER LIM
    IT OF ⍞''''MAX,, ',''
IT  IS NOT NECESSARILY GENUINE')
9]   →0
0]   (⍕'THE RESULTS ARE FOR THE 100TH TRIAL, IT
    IS NOT NECESSARILY THE BEST SET! '),⍕SF 2
1]   'FOR FURTHER ANALYSIS, TYPE ''GO'', ELSE PR
    ESS ''RETURN'' KEY'
2]   →('G'⍷□)/2+⍳26
3]   →0
4]   I←I+1
5]   TV←TV,(J0-⍴TV)⍴1
6]   FM←(J0)⍴FM,0⍴X←(J0)⍴X,0⍴BE←(J0)⍴BE
7]   →L13
 ∇
    TERM
```

```
   ▽SIM[□]▽
▽    SIM
     W←□ ,0⍴□ ←' ENTER BETA VALUE'
     X←□ ,0⍴□ ←'ENTER FREQ  MAX VALUE IN (HZ)'
     Y←□ ,0⍴□ ←'ENTER THE LOSS MAX (WITH CORRECT
     FACTOR CONSIDERED)'
     Z←□ ,0⍴□ ←'ENTER INTERVAL FOR LN FREQ VALUE
   S, I.E. .1'
     Z←□ ,0⍴□ ←'ENTER FREQUENCY LIMIT, I.E. 5 FO
   R LOG 5'
     J←Z⋄J1←Z
   JAY:J←J+Z
     J1←J1,J
     →(J≥Z)/END
□    →JAY
□  END:FNC
□    'THE CALC LOSS VALUES, ';LOSS;' ARE FOR LN
     F VALUES OF ';J1
□    →0
▽
   TERM
```